Nanoceram

Project n°.: COOP-CT-2004-507799

Project acronym: Nanoceram

Project title: Cutting tools and miniaturised parts with complex geometry based on nano powders

SIXTH FRAMEWORK PROGRAMME
HORIZONTAL RESEARCH ACTIVITIES INVOLVING SMES

CO-OPERATIVE RESEARCH PROJECT

Final Activity Report

Period covered: from 2004-08-01 – 2006-07-31

Date of preparation: September 2006
Start date of project: 1st August, 2004 Duration: 24 month

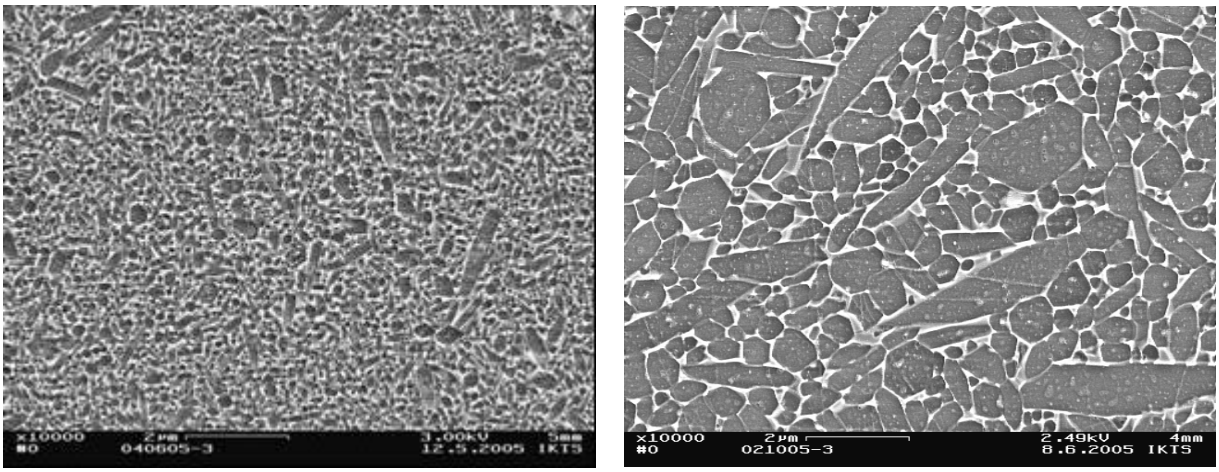
Project coordinator: Dr. Mathias Herrmann

Project coordinator organisation: Fraunhofer Gesellschaft / IKTS

1 Project objectives and major achievements during the project (publishable summery)

The aim of the project was to develop a technology for processing nanosized ceramic powders including the adaptations of shaping methods for prototypes as well as for small and large series.
The project was focused on applications of Si_3N_4 ceramics for wood cutting tools as well as Y-stabilised ZrO_2 materials for parts in medical technology, micro systems, micro reactors and sensors.

Nanotechnologies and nanomaterials have a perspective in a wide range of branches from mechanical engineering to medicine technology. Unfortunately, the development of nanomaterials is retarded by the lack of cost effective nanosized powders and suitable processing methods.
Nanopowders can normally not be processed by traditional powder metallurgical methods because of their high surface area and active interaction with the surrounding environment. NANOCERAM had tried to solve this problem by combining the modification of the powders during the powder manufacturing process and by adapting conventional powder processing methods. Beside the research institutes IKTS (Fraunhofer Institute for Ceramic Technologies and Systems), IVF (Industrial Research and Development Corporation Sweden) and RTU (Institute of Inorganic Chemistry of the Riga Technical University), the SME powder producer PCT (Plasma & Ceramic Technologies Ltd) and the SME ceramic component producers TKC (Technische Keramik GmbH), GOCERAM AB, FCT Ingenieurkeramik GmbH, Formatec Technical Ceramics BV as well as producers and users of ceramic tools like Johann Eberhard GmbH, Anton Peitz Zerspanungstechnik and DIAMONDE S.A.R.L. were involved in the project.
The nanosized Si_3N_4 and the ZrO_2 powders were produced by a plasma chemical process on pilot scale by PCT. The nanosized Si_3N_4 material contained the necessary sintering additives in the as synthesised state. This allows to crystallise the powder with minimal grain growth and to increase the stability against hydrolysis, to which all nonoxide nanopowders are subjected. RTU and PCT work at the start-up of continuous crystallisation equipment to deliver the nano Si_3N_4 powder in crystallised state, giving PCT a unique Si_3N_4 nanopowder quality on the world market. By using crystallised powders conventional powder processing and shaping methods could be successfully adapted.
In the project NANOCERAM a new nanocrystalline silicon nitride ceramic and the processing of Si_3N_4 nanopowders by CIP, gel casting and powder injection moulding were developed. A typical microstructure of ceramics produced from the nanopowder in comparison to that of a standard material is shown in Fig. 1-1. The mechanical properties in dependence on the shaping methods are given in Fig. 1-2.
Beside materials made from the pure nanopowder, materials were also produced from a mixture of 50% nanopowder and the commercial α-SN powder E10. The microstructure of these materials is nearly not altered in comparison to the materials from the pure plasma powder, but the strength could be increased (Fig. 1-3).



a) b)

Fig.1-1: SEM micrograph of an etched polished section of Si_3N_4 materials produced from nanopowder (a) and from conventional powder

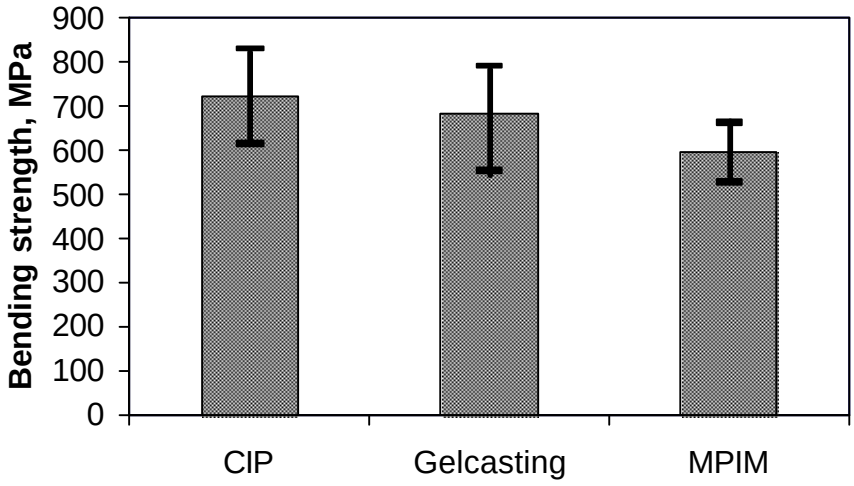


Fig.1-2: Comparison of the bending strength level of samples produced by different shaping methods from Si_3N_4 nanopowder sintered at 1575°C

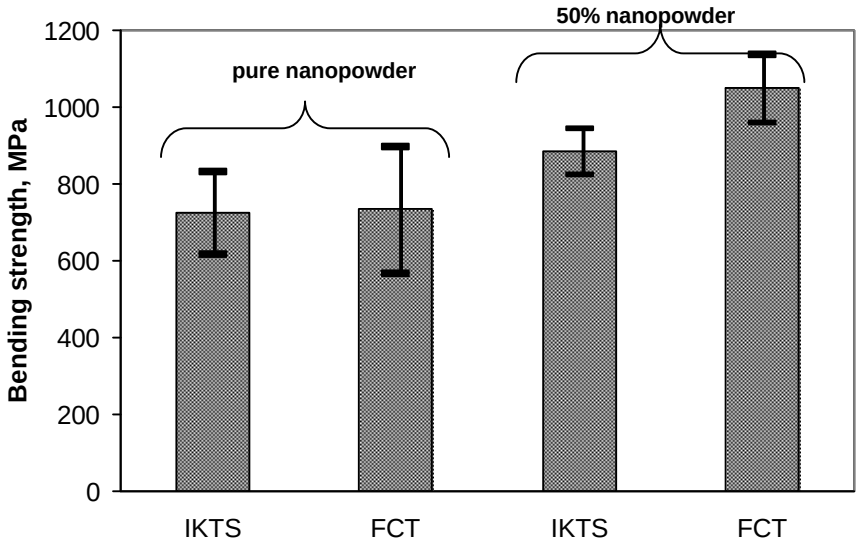


Fig. 1-3: Comparison of the bending strength of materials produced by IKTS and FCT from pure Si_3N_4 nanopowder and mixtures with a commercial α-Si_3N_4 nanopowder

The technology of nano silicon nitride materials was transferred to the SME partner FCT. On this base, nanosized materials with comparable or even higher strength in comparison to materials produced by IKTS could be produced by FCT (Fig. 1-2). The main reason for the higher strength level was the higher sintering temperature. The materials showed also improved tribological properties in comparison to standard materials.
Besides improved tribological properties, the new nano Si_3N_4 materials possess higher bending strength and an improved homogeneity of surface colour than the standard Si_3N_4 materials which FCT produce at present. In addition, a lower sintering temperature can be used as low as 1550°C in comparison to 1700-1900°C for standard Si_3N_4 materials. This results in energy saving, more homogeneous colour of the material and less wear of the furnaces. Because of these advantages FCT expect benefit of the production of nano Si_3N_4 materials for the application as cutting tools, saw teeth or wear parts (bearing components, cones, nozzles and rollers).

Different materials were tested in the project as cutting tools for wood working. Some of their properties are shown in Tab. 1-1. Two types of milling cutters were produced (Fig. 1-4): a metallic milling cutter with welded ceramic inserts and a full ceramic cutter.

The testing of the ceramic tools was driven by the increasing competition and cost pressure. The development in the furniture and wood industry results in the demand for high-speed-woodworking processes. This development results in higher demand for the wear resistance of the cutting tool. Up to now, hard metal (WC-Co) and polycrystalline diamond were used as cutting tools for the machining of these materials. Ceramic cutting tools are not used until today in wood and plastic industry.

Tab. 1-1: Properties of the ceramics tested as cutting tools for wood working

	Content of additives, wt.%	Sintering procedure	Bending strength, MPa	Hardness, HV10	Fracture toughness, MPam $^{1/2}$ 1)
H275 (FCT)	3	hot pressing	833 ± 85	1576	4.2
H200 (FCT)	8	gas pressure	781 ± 41	1600	4.6
A118 (FCT)	30% TiN	hot pressing	884 ±22	1476	5.8
T1102 (IKTS)	4.2	gas pressure	926 ± 89	1538	5.1
Alpha SiAlON (IKTS)	2	gas pressure	765 ±48	1739	5.4
PP169 (IKTS)	14	gas pressure	756±120	1522	4.5

1) measured from the crack length after Anstis

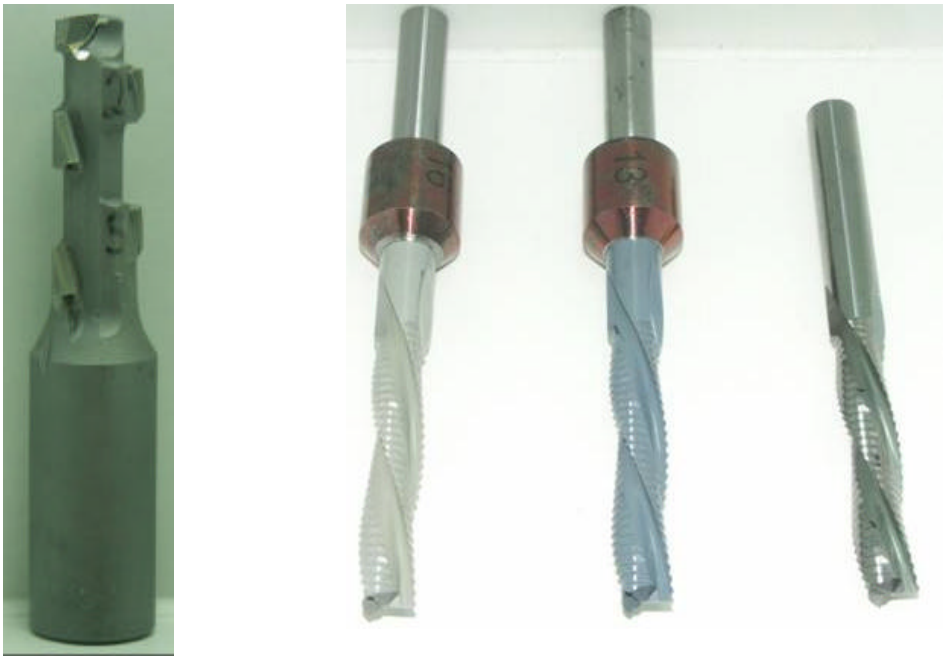


Fig. 1-4: Types of milling cutters produced in the project

The different milling cutters were tested in milling of chipboard, MDF board, strong melamine with hard inclusions and massive wood. In all cases cutting edges from ceramics showed strong flak spalling after milling. In comparison cutting edges from hard metal show only chamfering. An improvement of the wear behaviour can be expected by adapting the geometry of cutting edges. An increased lip angle can reduce the formation of cracks at the brittle ceramic cutting edges. The use of massive ceramic milling cutters can not be recommended due to the high material costs. In future ceramic cutting inserts will be used which are assembled at the metallic carrier by clamped joints. Especially the saw blades with removable inserts from nano Si_3N_4 ceramics look promising despite of the lack of tests. The testing of cutting tools with improved geometry of the cutting edge will be continued by the partner Johann Eberhard GmbH, DIAMONDE S.A.R.L. and Anton Peitz Zerspanungstechnik.

The conducted wood working tests with nano Si_3N_4 are not yet sufficient for a transfer into production at this stage. However, the project showed that nano Si_3N_4 can be manufactured using different shaping methods. Dense parts could be produced via shaping by CIP, gel casting and injection moulding (MPIM, PIM) using nano silicon nitride powder with high bending strength. The developed feedstock and the MPIM technology using Si_3N_4 nanopowder will be used by FCT, Formatec, Goceram and TKC.

For materials based on nano zirconia powder produced by PCT in this project a commercial use is not expected. The zirconia powder delivered by PCT showed a broad grain size distribution. Beside nanosized particles coarse particles >2µm were detected which form coarse grains in the sintered material (Fig. 1-5).

Therefore, the project consortia looked at the market for an alternative fine dispersed zirconia powder doped with Al_2O_3 which can be used for the production of the special thin-walled parts for medical technology. In the last time, Tosoh has put fine zirconia powders with 14m^2/g on the market. Besides the zirconia TZ-3Y-E doped with 3mol Y_2O_3 and 0.25% Al_2O_3, the zirconia TZ-3Y-20A with 3mol Y_2O_3 and 20%Al_2O_3 are interesting for our application. These powders were supplied by Tosoh as powder or as granulate. In comparison the qualities of Tosoh with 7m^2/g were investigated. For both fine powders from Tosoh freeze granulate and a feedstock for MPIM was developed and shaped via CIP or injection moulding. The parts made from the finer powder with 0.25% Al_2O_3 could be densified at a 50°C lower temperature in comparison to the coarser standard quality and possess a finer microstructure and higher bending strength than the standard quality (Fig. 1-6). The properties of the freeze granulate were not as good as the granulate supplied by Tosoh and the materials made from it showed a lower bending strength. The spray granulate using the zirconia grade B, produced by PCT, could not be fully densified even at 1600°C and showed a very low level of bending strength.

TKC has used the fine disperse zirconia powders for the production of small parts with fine microstructures. On the basis of the investigations, TKC is able to produce thin-walled parts (1.5mm< thickness <4mm) with sintering densities >99% using fine grained Tosoh zirconia via pressing and injection moulding technology for application in medical technology.

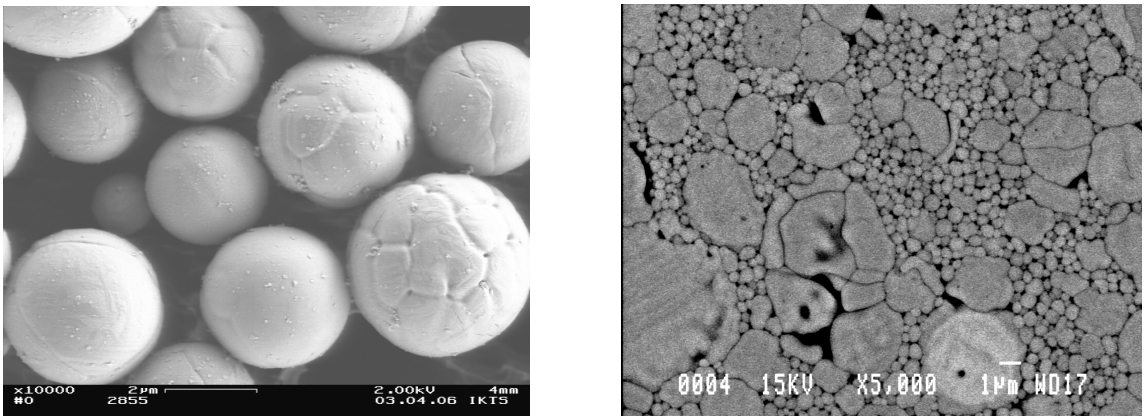


Fig.1-5: Coarse zirconia particles > 2µm in the powders produced by an plasma chemical process and SEM image of the material produced from this powder (sintered at 1500°C by IVF)

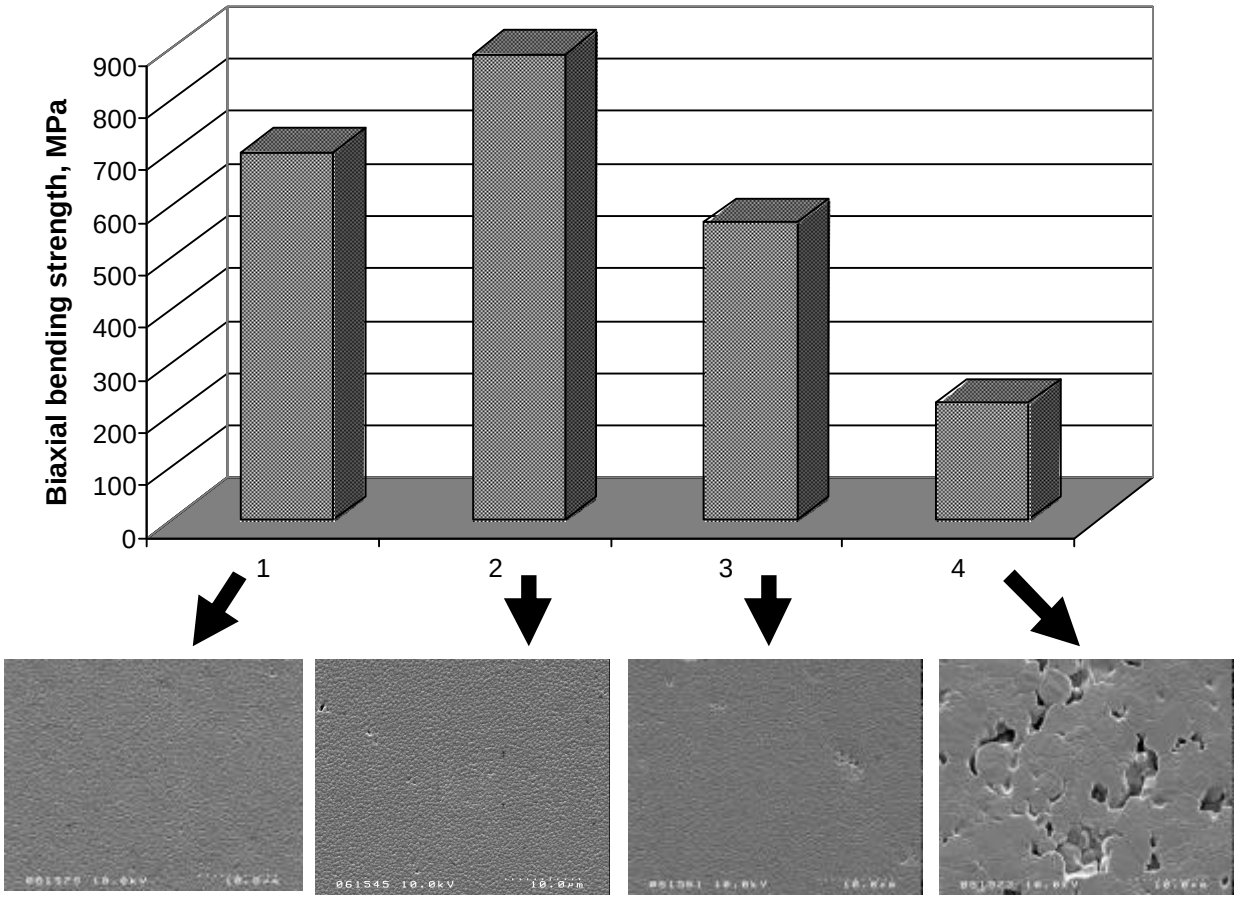


Fig. 1-6: Biaxial bending strength and microstructure of sintered materials using different zirconia granulates

Powder / granulate used:

1	TZ-3YSB-E ($7m^2/g$)	spray granulate of Tosoh
2	TZ-3YB-E ($14m^2/g$)	spray granulate of Tosoh
3	TZ-3Y-E ($14m^2/g$)	freeze granulate of IVF
4	grade B ($25m^2/g$)	spray granulate of RTU

2 Workpackage progress of the period 2005-08-01 – 2006-07-31

Table 2-1: Deliverables List

Deliverable No	Deliverable title	Delivery date (proj. month)	Actual delivery date (proj. month)	Nature	Dissemination level	WP no.	Lead partiCIPant	Estimated person-months
DO	Plan for using and disseminating knowledge	2	5	O	RE	9	IKTS	0,25
D1	Demands for cutting materials from Si_3N_4	2	5	O	RE	1	IKTS	0,7
D2	Determination of detailed geometry of the cutting tools	2	5	O	RE	1	IKTS	0,58
D3	Demands for materials from ZrO_2	2	5	O	RE	1	IKTS	0,7
D4	Determination of detailed geometry of the parts for medicine technique	2	5	O	Re	1	IKTS	0,59
D5	Delivery of 6kg silicon nitride powder	2	4	O	PU	2	PCT	1,25
D6	Delivery of 4kg ZrO2 powder	4	6	O	PU	2	PCT	1,25
D7	Surface modification of Si_3N_4 powder in water to prevent hydrolysis Surface modification of Si_3N_4 powder in water to prevent hydrolysis	4	4	O	RE	3	IKTS	2,5
D8	Surface modification of Si_3N_4 powder in organic medium and IR-experiments for MPIM	5	5	O	RE	3	IKTS	1
D9	Batch of ZrO_2 prepared by dry processing	6	7	O	RE	3	RTU	3

R1	Report to EC	6	6	R	CO	9	IKTS	0,1
D10	Delivery of 10kg silicon nitride powder	7	10	O	PU	2	PCT	1,25
D11	Torque rheometer results of Si_3N_4 powder in thermoplastic suspensions	7	7	O	RE	3	IKTS	0,5
D12	Adsorption experiments and characterisation of the Si_3N_4 powder surface in water for gelcasting	8	8	O	RE	3	IKTS	1,0
D13	First charge of ZrO_2 suspension in water suited by spray drying	8	10	O	RE	3	RTU	2,0
D14	Batch of ZrO_2 prepared by wet -processing	8	10	O	RE	3	IVF	1,57
D15	Manufacture of finihed prototypes on the base of standard Si_3N_4	8	9	P	PU	7	IKTS	3,00
D16	Manufacture of prototypes on the base of standard ZrO_2	8	9	P	PU	7	DICERAM	0,36
D17	Pressing and characterisation of ZrO2 parts produced by using spray and freeze granulat	8	10	O	PP	4	DICERAM	1,1
D18	Delivery of 6kg ZrO2 powder	9	10	O	PU	2	PCT	1,25
D19	PIM equipment and technology for Si_3N_4	10	10	O	PU	4	IKTS	0,8
D20	Shaping experiments of ZrO_2 test bars by MPIM	10	10	O	PP	4	IVF	3,3
D21	Characterisation of prototypes on the base of standard Si_3N_4	10	10	O	PU	7	IKTS	0,37
D22	Characterisation of prototypes on the base of standard ZrO_2	10	10	O	PU	7	IKTS	0,3

D23	Delivery of 10kg ZrO2 powder	11	15-19	O	PU	2	PCT	2,0
D24	Thermal analysis of injection moulded Si_3N_4 parts	12	12	O	RE	5	IKTS	0,4
D25	Debindering procedure for injection moulded ZrO_2 parts	12	13	O	RE	5	IVF	0,68
D26	Tests of the prototypes based on standard Si_3N_4	12	22	O	PU	8	FCT	0,7
R2	Midterm meeting and report	12	12	R	CO	9	IKTS	0,1
D27	Preparation of a Si_3N_4 slurry for gelcasting	13	12	O	RE	3	IKTS	0,36
D28	Preparation of a Si_3N_4 feedstock for MPIM	13	13	O	RE	3	IKTS	0,5
D29	Shaping experiments for cylindrical green bodies and test bars by gel casting of Si_3N_4	14	14	O	RE	4	IKTS	1,0
D30	Optimisation of geometry and cutting conditions for Si_3N_4 prototypes	14	14…23	O	PP	8	Eber-hard	0,5
D31	Tests of the prototypes based on standard ZrO_2	22	22	O	PU	8	TKC	0,6
D32	Delivery of 3,5kg ZrO_2	20	20	O	PU	2	PCT	1,86
D33	Second batch of a ZrO_2 suspension in water suited for spray drying	15	18	O	RE	3	RTU	8,43
D34	Preparation of a Si_3N_4 feedstock composition suited for PIM	20	17	O	RE	3	Forma-tec	1,93
D35	Development of drying procedure, characterisation of green compacts made by gel casting	16	16	O	RE	4	IKTS	0,3

D36	Shaping experiments of Si_3N_4 test bars by MPIM	16	16	O	RE	4	IKTS	1,0
D37	Shaping of Si_3N_4 prototypes by MPIM and mould construction	22	22	O	RE	4	IKTS	1,5
D38	Debindering procedure for injection moulded Si_3N_4 parts	16	16	O	RE	5	Forma-tec	0,59
D39	Technology transfer to FCT	22	22	O	RE	6	FCT	3,26
D40	Technology transfer to TKC	22	-	O	RE	6	TKC	2,80
D41	Optimised shaping and drying procedure for gel casting of Si_3N_4	18	18	O	CO	4	IKTS	0,2
D42	Characterisation of Si_3N_4 parts produced by MPIM	18	18	O	PP	4	IKTS	0,69
D43	Preparation of a optimised granulate of ZrO_2	19	18	O	RE	4	RTU	7,43
D44	Characterisation of ZrO_2 parts produced by MPIM	18	18	O	PP	4	IVF	1,78
D46	Sintered Si_3N_4 prototypes based on nano Si_3N_4	18 (CIP) 22 (MPIM)	18 (CIP) 22 (MPIM)	P	PP	5	FCT	0,93
D47	Sintered Si_3N_4 prototypes	22	22	P	PP	5	Forma-tec	0,99
R3	Report to EC	18	-	R	CO	9	IKTS	0,1
D48	Characterisation of prototypes on the base of nano Si_3N_4	23	24	O	PP	5	IKTS	0,5
D49	Characterisation of prototypes on the base of nano ZrO_2	23	23	O	PP	5	IVF	0,42

D50	Cutting tools from nano Si_3N_4	20	20	P	PP	6	Eber-hard	2,85
D51	Production of ZrO_2 prototypes	22	23	P	PP	6	TKC	1,14
D52	Tests of the prototypes based on nano Si_3N_4	22 CIP 24 MPIM	22 CIP -	O	PP	8	Dia-monde	0,73
D53	Tests of the prototypes based on nano ZrO_2	24	24	O	PP	8	TKC	0,43
D54	Regulation of work shops with partners and their costumers	24	-	O	PU	9	IKTS	0,1
D55	Comparison of the tests with Si_3N_4	24	24	O	PP	8	Diamonde	0,54
D56	Comparison of the tests with ZrO_2	24	24	O	PP	8	TKC	0,33
R4	Final meeting and 24 month report and final version of plan for using and disseminating knowledge	after 24	24-25	R	PP	9	IKTS	2,0

Milestones and expected result

Milestone N°	task	State of completion
M1 (2. Month)	In the kick off meeting these first results will be discussed with all partners. The tasks and objectives will be concretised for each partner.	fulfilled
M2 (8. Month)	Properties of the Si_3N_4 powder : phase content : ß/(α+ß) ≥ 70 % ; crystallite size ≤ 70 nm; Properties of the ZrO2 powder: Phase content : m/(t+c+m) < 20 %; crystallite size size ≤ 70 nm	fulfilled parameter fulfilled but too large distribution of particles
M3 (13. Month)	Si_3N_4 slurry suitable for gelcasting with a powder loading of 40- 50Vol% Development of Si_3N_4 feedstock for MPIM with a powder loading of 40-50Vol%	fulfilled fulfilled
M4 (14. Month)	Determination of the geometry and cutting conditions for Si_3N_4 prototypes	fulfilled
M5 (20. Month)	Development of ZrO_2 suspension in water suited for spray and freeze drying Development of Si_3N_4 feedstock composition suited for MPIM with a powder loading of 40- 50Vol%	fulfilled fulfilled
M6 (22. Month)	Sintered prototypes base of nano Si_3N_4 with a density >99% theoretical density; Sintered ZrO_2 prototypes with a density >99% theoretical density	fulfilled fulfilled
M7 (23. Month)	Cutting tools from nano Si_3N_4 with the necessary mechanical properties and geometry; ZrO_2 prototypes with the necessary mechanical properties and geometry with the necessary mechanical properties and geometry (Determined at M4)	fulfilled fulfilled
M8 (24. Month)	Test results of prototypes based on nano Si_3N_4 and nano ZrO_2	not finished yet

2.1 Acquisition phase – workpackage 1

PartiCIPant involved	Diceram	Goceram	FCT	Eberhard	Peitz	IKTS	IVF

Objectives

Acquisition of data about the application of wood working tools and parts for medicine technique

- Acquisition of data for the conditions, under which materials will be applied as tools for wood milling, sawing; collecting information about mechanical, thermal and chemical loads
- Collecting information about mechanical and chemical loads of ZrO_2 ceramic parts for medicine technique based on the user profile

Definition of design of prototype and test parts

Progress

The following geometries and materials were agreed:

Si_3N_4 based material:

Ceramic inserts for cutters (standard and nano Si_3N_4)

Saw teeth (nano Si_3N_4)

Full ceramic cutter (standard and nano Si_3N_4)

ZrO2 based material:

Different thin walled parts, which were used in the endoscopy (standard and nano Si_3N_4)

After the bank rupture of Diceram the prototypes from zirconia powder had to adapt to the range of products of the new partner TKC.

Deliverables, Milestones

D0: The first draft of the plan of using and dissemination of knowledge was accepted by all partners at the first project meeting and was updated during the project.

D1-D4: The demands and geometries of the prototypes from nano Si_3N_4 and ZrO_2 were determined at the first project meeting and updated during the project.

M1: The first project meeting took place on the Materialica in October 2004. On the meeting the first steps of work were discussed. In January 2005 a meeting took place in Dresden. On the meeting the achieved results and the working steps for the following period were discussed.

Deviations /Problems

The workpackage 1 ran nearly in the given time schedule. Some delays take place due to the real start of the project in September/October 2004. But these delays could be diminished. An adaptation to the range of products of the new partner TKC was necessary after the banc rupture of the former partner Diceram.

2.2 Powder Preparation – work package 2

PartiCIPant involved	PCT	RTU						

Objectives

Supply of different powder batches in required quality and quantity

Progress

Four batches of plasma processed silicon nitride powders with a high content amorphous phase were delivered by PCT during the running project. To improve the processing a crystallisation in presence of oxynitride phase had to conducted. The TU Dresden has been conducted the crystallisation and jet milling of powders by order of RTU.
PCT produced and delivered a total of 20kg of ZrO_2 doped with 5,2±0,3 wt.% of Y_2O_3 and 0,3±0,1 wt.% of Al_2O_3, specific surface area 19 - 30±3 m^2/g in accordance with the work plan and agreement with the corresponding project partners during the reporting period. The phase composition and crystallite size of the zirconia powder grade B was measured by the Rietveld analysis and compared to the fine zirconia powder TZ-3Y of Tosoh. The Tosoh powder possesses nearly the same phase composition and crystallite size in the range between 20 and 30nm as the powder of PCT. Using a special analysis for measurement the grain size distribution besides nanosized particles a high amount of coarse particles >2µm were detected in the powder grade B.

Deliverables

D5: PCT delivered 6 kg Si_3N_4 (Y_2O_3 – Al_2O_3-doped) within the first 6 month to IKTS.

D6: 4 kg ZrO_2 doped with Y_2O_3 and Al_2O_3 were delivered within the first 6 month according the work plan by PCT. 2 kg ZrO_2 was used by RTU for spray granulation and 2 kg ZrO_2 were used by DICERAM.
D10: 10 kg silicon nitride powders were delivered to IKTS in May 2005.

D18: 3 kg ZrO_2 were delivered to RTU for investigations of suitable surfactants (February 2005 and June 2005), 2kg ZrO_2 were delivered to IVF (June 2005) and 1kg powder was delivered to Formatec in August 2005.

M2: The quality of the Si_3N_4 powder and ZrO_2 powder were tested by Rietveld analysis in the IKTS. The following properties were reached:

Table 2.2-1: Results of the Rietveld analysis for Si_3N_4 powder after crystallisation

powder	ß/(α+ß), %	Crystallite size of ß-phase, nm	BET, m^2/g
goal	= 70%	= 70nm	
AY4/32and AY4/33	73	35	17
AY5/15 and AY5/16	80	35	15

Table 2.2-2: Results of the Rietveld analysis for ZrO_2 powder

powder	tetragonal and cubic forms of ZrO_2, %	monoclinic form of ZrO_2, %	Crystallite size of tetragonal form, nm
goal		< 20%	= 70nm
ZrO_2-Y-Al/4/42	86,1	13,9	35
ZrO_2-Y-Al/5/25	81,9	18,1	27
ZrO_2-Y-Al/5/22	92,6	7,4	26
ZrO_2 TZ-3Y Tosoh	89	11	22

D32: PCT delivered the last 3.7 kg zirconia powder in the 20th project month. With it the determined amounts of zirconia powder were delivered by PCT within the project.

Deviations /Problems

Our partner RTU took over some key functions for pre treatment of the nano Si_3N_4 - powders. Continuously working crystallisation equipment attached to the plasma reactor should deliver plasmachemical powder in suited particle size distribution and quality. Because of technical problems the assembly of the continuous crystallisation equipment has not finished during the project. The partner RTU should start up this new technological equipment and evaluate the quality of the silicon nitride powder as crystallized. This modification also affected the industrial partner PCT. PCT should proceed the crystallisation of the plasmachemical powder to produce the required amount of powder as crystallized. All these modifications were related to tasks in the workpackage 2. On behalf of the supply of powder for the RTD up to now silicon nitride powder had to be crystallised by the RTD performer IKTS. This discontinuous batch procedure is more expensive than the continuous crystallisation and additional expenses arose for IKTS. In the first year IKTS needed a capacity of 2.78 man months or 17750 EURO for the crystallization of 20kg plasmachemical powder. For the second year we have plant the delivery of 10kg crystallized silicon nitride powder. The TU Dresden had been conducted the crystallisation and jet milling of powders by order of RTU.

The zirconia powder as delivered by PCT possesses a broad particle size distribution. Besides nanosized particles a high amount of coarse particles >2µm were detected in the powder which form coarse grains in the sintered material (fig. 2.1-1, 2.1-2).

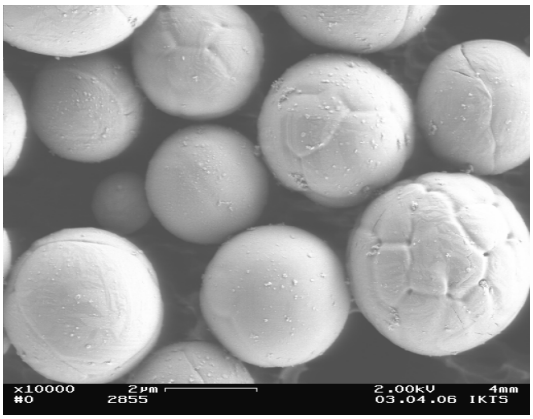


Fig.2.2-1: Coarse particles > 2µm in the Zirconia powder grade B

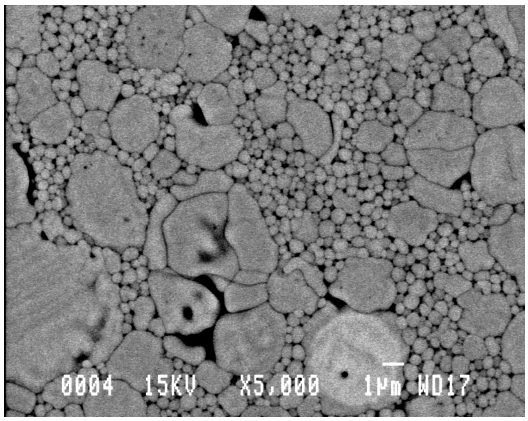


Fig.2.2-2: Microstructure of a sample from ZrO2-Y-Al powder grade B sintered at 1500°C by IVF

Two possible reasons can be seen for the formation of coarse particles in the zirconia powder grade B of PCT:

- The broad particle size distribution of raw powders does not allow complete introduction of particles into the centre of high temperature gaseous flow. The coarse particles are not transferred in the hot area of the reactor.
- The consolidation of fine particles in high temperature gaseous flow.

An improvement of the quality of plasma chemical produced zirconia powder could not be reached by PCT during the project. Further investigations are necessary. A discussion about the possibilities of an effective production of ZrO_2 powders by plasmachemical methods took place. Based on the existing results and calculations of the costs a production of a competitive powder seems not be possible.
Therefore the partially stabilized zirconia powder TZ-3Y-E (5.26 wt% Y_2O_3, 0.25 wt% Al_2O_3, BET 14.8 m^2/g) and TZ-3Y-20A ((3.97 wt% Y_2O_3, 21.27 wt% Al_2O_3, BET 13.6 m^2/g) delivered by Tosoh were used in the further investigations in agreement with the partners. These powders contain crystallites in the same range as the powder grade B. The TZ-3Y-E powder was developed to sinter at a lower sintering temperature as the coarser powder TZ-3YS-E with 7m2/g to deliver a fine nanostructured microstructure. The powder TZ-3Y-20A containing 20% Al_2O_3 has to densify in a combined sinter HiP process to get a fine microstructure and high bending strength. Both zirconia powders can be used for the production of parts for the medicine technique.

2.3 Surface modification – work package 3

Participant involved	GOCERAM	IKTS	IVF	RTU

Objectives

Surface modification of the nanosized powders to achieve high solid load and well dispersed particles in the suspension /feedstock for selected shaping methods.

Progress

The investigations concerning surface modification of nanopowders were finished with promising results. In the result slurries in water and organic medium could be generated which are suitable for the production of different granulates or feedstocks.

Surface modification and preparation of spray granulates from zirconia powder

A detailed analysis of the surface properties and the adsorption behaviour of the plasma chemically produced ZrO_2 powders in comparison to commercial powders were carried out by RTU. This analysis showed that by using appropriate surfactants the surface properties of the plasma chemical powder can be shifted to the properties of the Tosoh powder. Also the aging behaviour of suspensions was investigated and mechanisms proposed. The investigated surfactants – KD7 and Zephrym – ensure the steric stabilization and high solid loading in suspensions of zirconia powders apart from the acidic or basic character of dispersion medium and anionic (KD7) or cationic (Zephrym) character of the surfactants

Preparation of a slip for freeze granulates from zirconia powder

Slips were prepared by planetary milling from different batches of plasma powder grade B with a BET specific surface area between 19.5 and 27.5 m^2/g. The solids loading as well as the amount of dispersant were adapted so a fluid slip could be achieved at as high powder content as possible. For this 4 wt% dispersant (KD7, PAA/PEG copolymer) was required at a powder loading of 27.6vol%. Additional 5vol% latex was used as binder. Produced nano-ZrO_2 (Grade B) contained large dense agglomerates that give rise to a bimodal microstructure and is considered unfavourable for the mechanical performance. Therefore in addition commercial powders from Tosoh was evaluated and processed by freeze granulation.
In difference to zirconia powder grade B polyacrylates were used for dispersing of zirconoa powder of Tosoh due to PAA/PEG comb polymer does not work properly. Dolapix PC75 was found for TZ-3Y-E and PC21 for TZ-3Y20A as dispersant showing the best properties in the slip for freeze granulation. Additionally, pH adjustment with NH_3 showed a positive respond by a decreased viscosity level. The powder loading in the slips was 35vol%. After conditioning over night the slips were sieved 31.5 µm and then it was added 6 vol% PVA and 1.5 vol% PEG400 based on solids as binder. The slip was mixed by impeller stirring for 3 hours and sieved 250 µm prior to granulation.

Preparation of feedstocks for MPIM from zirconia powder

The feed stock using zirconia powder grade B possesses an insufficient solids loading (43 vol%). Even components with very thin-walls showed severe cracking at de-binding process and poor sintering performance (≈93% of theoretical density) in the investigations of Goceram and IVF. A pre-treatment of Grade B by ball milling in organic solvent followed by freeze granulation showed only pure improvements in subsequent feed stock preparation.

RTU has developed a feed stock for MPIM of ZrO_2 powder grade B with a solid content of 53vol% what is much better than the results achieved by Goceram.
The feedstock in tab. 2.3-1 was developed by RTU but the sinter ability was not investigated. The investigations were stopped due to all zirconia powder batches of PCT contained large dense agglomerates.

Tab. 2.3-1: feedstock for MPIM of zirconia powder grade B

composition	amount
Zirconia powder grade B	53vol%
Paraffin wax	47vol%
Hypermer LP1	1.5wt% (related to the powder amount)

In sum it was difficult to disintegrate the powder batch using zirconia grade B of PCT before freeze granulation or MPIM due to hard agglomerates are contained. This is a reason of importance for the exaggerated grain growth observed after sintering.
Therefore feedstocks using the fine powders TZ3Y-E and TZ3Y-20A were developed additionally for MPIM by GOCERAM and TKC.
Goceram has developed in cooperation with IVF a feedstock for MPIM. The zirconias were processed in cyclohexane by ball-milling using 0.2wt% stearic acid. The different feedstocks have been prepared using the identical procedure as those for the PCT zirconia. At first the mixture of the organic components was melted at maximum 120°C and then small quantities of the powder were added under mechanical low-shear mixing until reaching a viscosity corresponding to a mouldable condition. 87 wt% paraffin and 13 wt% of a special basic additive were used as binder system. The solid content of the mouldable feedstock was 46vol%. Both Tosoh powders reached in general 5 – 7 % higher solids content compared to the PCT powders despite comparable BET specific surface areas. In the result the feedstocks based on the powders TZ-3YE and TZ-3Y-20A pre-processed in cyclohexane and basic additive can be used for MPIM of components selected by the project partners for testing and sintered to the full density.
In addition TKC investigated the surface modification of zirconia grade B of PCT and of the following powders of Tosoh:

Tab.2.3-2: Zirconia powders shaped by MPIM and solid content in the feedstocks (results of TKC)

	supplier	Content of Y_2O_3, wt%*)	Content of Al_2O_3, wt%*)	BET,m^2/g*)	Crystallite size, nm*)	Solid content in the feedstock, vol%
TZ3YS-E	Tosoh	5.4	0.25	7	30	46,65
TZ3Y-E	Tosoh	5.4	0.25	14	20	42,84
TZ3YS-20A	Tosoh	5.4	20	7	30	49,64
TZ3Y-20A	Tosoh	5.4	20	14	20	45,80

* dates of the supplier

The coarser powders TZ3YS-E and TZ3YS-20A were investigated in comparison.
In the result a feedstock consisting from paraffin and a mixture of long-chain carboxylic acid and aldehyde was used. On this base solid contents between 42.8 and 49.6vol% could be reached for the different zirconia powders of Tosoh (tab.2.3-2). Using the same binder composition for the zirconia powder grade B only feedstocks with a maximal solid content of 35vol% could be generated by TKC.

Preparation of feedstock for MPIM from nano Si_3N_4 powder

Good mouldable feedstocks for MPIM were developed by IKTS using pure plasma powder and a mixture with 50% plasma powder and SN-E10 powder. The feedstock of the mixture with 50% plasma powder and SN-E10 powder contains 48,5vol% solid and was used for the production of prototypes.

Preparation of slurry for gelcasting from nano Si_3N_4 powder

The development of gelcasting using pure plasma powders or a mixture with SN-E10 powder was finished. Slurries with a solid content of 41 vol% deliver homogeneous green bodies and full dense sintered bodies.

Deliverables / Milestones

D7: "Surface modification of Si_3N_4 powder in water to prevent hydrolysis"

RTU characterized the surface properties of plasma-produced silicon nitride by potentiometric titration and electrokinetic measurements in dilute aqueous suspensions. The titration of silicon nitride plasma powders exhibits the presence of weak bases (aminogroups) and weak acids (silanol groups) on the powder surface. Some kinds of surfactants (aminoacid, alkanolamine, polymer (acidic and basic), polyelectrolyte and copolymer with a polyelectrolyte backbone) were investigated with regard to their effect on the charge properties of the silicon nitride surface in water by RTU.
The Si_3N_4 plasma powder was stabilised in the aqueous suspension by adsorption of 2-amino-propionic acid (APA) and 2-amino-2-methyl-1-propanol (AMP) by IKTS. The best results with respect to stability of suspension were obtained with amino-methyl-propanol (AMP). Based on these results gelcasting slurries of crystallized nano Si_3N_4 powders were prepared.

D12:"Adsorption experiments and characterisation of the Si_3N_4 powder surface in water for gelcasting"

Adsorption isotherms were performed for AMP, PAA and KD7 in dilute aqueous suspensions by IKTS. PAA demonstrates the adsorption of high affinity type. The adsorbed amount reached a plateau of 0.45 mg/m^2 of silicon nitride. The plateau value is of 0.6 mg/m^2 for KD7 (comprised on a PAA backbone). AMP shows weakly increasing isotherm far from the line, which represents 100% adsorption.
Further experiments were carried out for the surface modification of Si_3N_4-powder by adsorption of silanes. Especially the adsorption of n-propyltriethoxysilane (PTEO) was investigated. This adsorption yields to a hydrophobic powder surface. Using an amphilic surfactant the silane modified powder can be well dispersed in aqueous suspension. The results are a higher solid volume content of suspensions and the powder is more stable against hydrolyses.

D8: "Surface modification of Si_3N_4 powder in organic medium and IR-experiments for MPIM"

Suitable to silicon nitride nano-powder surface active substances and their mixtures have to be selected by sedimentation experiments in non-polar solvents and DRIFT-spectroscopy of surface. Suitable surface active agents were determined. These results are the base for feedstock development.

D11: "Torque rheometer results of Si_3N_4 powder in thermoplastic suspensions"

Based on the sedimentation and DRIFT – investigation a binder composition was proposed. The nanosized powder was milled in a planetary mill before adding to the thermoplastic binder. The surfactant of the binder composition was added to the hexane suspension for better adsorption conditions. After milling the powder was dried to constant weight.
The binder consisted of paraffin wax, fatty amine C_{18} and a surfactant. A solid content of 76.0 wt % corresponding to a volume packaging of approximately 46.9 % was achieved.
Rheological properties were investigated with stress controlled rotation viscosimeter. The viscosity of 15 Pas is suitable for medium pressure injection moulding.

D13: "First charge of ZrO_2 suspension in water suited by spray drying"

The effect of surfactants on maximal solid loading of aqueous zirconia suspensions was studied by RTU. A maximal solid content of 70-72 wt% is achieved with KD7 in water and with ATSURF 3222 in water. The comparatively high solid loading is also obtained with ammonium citrate in basic medium. The optimal concentration of KD7, ATSURF 3222 and ammonium citrate were performed by viscosity measurements.
The first batch of zirconia suspension in water with ammonium citrate as surfactant for spray draying was prepared by RTU and 2kg were delivered to DICERAM. It was demonstrated that spray-drying granulate has a good flowability and an increased bulk density in comparison with the as-prepared powders from plasma manufacturing equipment (apparent bulk density increases from 0.2 to 1.6 g/cm^3, tapped bulk density increases from 0.4 to 1.6 g/cm^3).

D9: "Batch of ZrO_2 prepared by dry processing"

In particular, it was intended to utilize dry pre-processing route to modify the particle surfaces and at the same time break down agglomerates which easily form in nano particle powders. Novel pre-processing additives were evaluated which will be tailored to interact with the nano particle surface.
Initially, feedstocks based on 25 vol% as-received Grade B (density 5.81 g/cm^3) was prepared by GOCERAM with or without acid (A) or basic surfactant (B) by mixing with the wax composition. Additional the as-received powder was heat-treated to 700°C the purpose being to ensure removal all kinds of organics from the surface which could impair the dispersion in the wax-based system. This heat treatment resulted in a slight increase of BET surface area and slight decrease in density, from 5.81 to 5.75 g/cm^3. The treatment did not lead to any significant effect in terms of improved dispersability and solid load.

D14: "Batch of ZrO2 prepared by wet –processing"

After wet pre-processing with respective surfactants feedstocks with higher solid loadings were possible. Based on the previous viscosity measurements the maximum mouldable composition was tested by GOCERAM. A solid loading of 44vol% was achieved. With this loading a lot of different shapes could be made without any problem.

D33: "Second batch of a ZrO_2 suspension in water suited for spray drying"

RTU performed developing a zirconia (grade B) suspension suitable for spray drying. On this base RTU produced a second batch in January 2006 which were used for producing 0,9kg

spray granulate. This granulate were sent to TKC and tested with the technology of CIP and sintering by TKC.

M3 (13. Month): Si_3N_4 slurry suitable for gelcasting with a powder loading of 40-50Vol%

With the following slip composition was developed by IKTS which contains 41vol% nano Si_3N_4 composite powder:

Tab.2.3-3: Slip composition for gelcasting of nano Si_3N_4 powder

composition gelcasting slurry	**volume percent**
S_3N_4-plasma powder	41,0
monomer (methacrylamid)	7,9
crosslinker (methylendiacrylacidamide)	1,7
dispersant	0,8
defoming agent (nonylalcohole)	0,16
water	48,4
initiator (addition directly before casting)	0,04

M3 (13. Month): Development of Si_3N_4 feedstock for MPIM with a powder loading of 40- 50Vol%

A binder composition was provided by IKTS, including paraffin wax (82.6 wt %), fatty amine C18 (6,3 wt %) and Lubrizol 2153 (11.1 wt %). The solid content: of the feedstock is 77,2 wt% and 48,5vol% respectively. The feedstock possesses an apparent viscosity of 10Pas and ensures a good process ability by MPIM technology. The developed feedstock was used for manufacturing saw teeth.

M5 (20. Month): Development of ZrO_2 suspension in water suited for spray and freeze drying

The following zirconia suspension was developed for spray granulation by RTU:

Tab. 2.3-4: Zirconia suspension for spray granulation

Suspension concentration, wt. %	50-52
Surfactant	KD 7
Content of surfactant, wt. % in relation to powder	3

Using this slip the following spray granulate charges were produced for the project partners:

Tab. 2.3-5: ZrO_2 spray granulate produced by RTU

Charge No	**Weight, kg**	**Project partner**	**Date**
ZrO2-Y-Al-5/37-45/165-168 G	0,77	Formatec	November 2005
ZrO2-Y-Al-5/37-45/165-168 F	0,62		
ZrO2-Y-Al-5/41;52/175-177 G	0,90	TKC	January 2006
ZrO2-Y-Al-5/41;52/175-177 F	0,90		

IVF developed the following slips with different zirconia powders which are suited for freeze granulation:

Tab. 2.3-6: Slips for freeze granulation of different zirconia powders

Powder	BET (m^2/g)	Dispersant	Dispersant (wt%)	Binder	Binder (vol%)	Solid content* (vol%)
Grade B (PCT)	27,5	PAA/PEG KD7	4	Latex	5vol%	25,6
TZ-3Y-E (Tosoh)	14,8	PAA Dolapix PC75	0.6	PVA/PEG	7,5vol%	35
TZ-3Y-20A (Tosoh)	13,6	PAA Dolapix PC21	0.6	PVA/PEG	7,5vol%	35

*Prior to binder addition

M5 (20. Month): Development of Si_3N_4 feedstock composition suited for PIM with a powder loading of 40- 50Vol%

Based on the results to the developing of a feedstock for MPIM in the milestone M3 0.5kg feedstock using a mixture containing 50 % nano powder was prepared for PIM experiments by IKTS. Formatec tested the Si_3N_4 feedstock with a mould to produce test bars and a mould for a small complex shaped valve (fig.2.3-1). Injection moulding, debinding and sintering was performed with good result.

Fig. 2.3-1: Valve from nano Si_3N_4 material produced by PIM (high pressure injection moulding)

2.4 Shaping methods – workpackage 4

Parti CIPant involved	TKC	GOCERAM	FORMATEC	IKTS	IVF	RTU

Objectives:

Development of the selected shaping methods for the production of prototypes using nanosized Si_3N_4 and ZrO_2 powders.

Progress

Gelcasting of nano Si_3N_4 composite powder

A gelcasting procedure was developed by IKTS (fig. 2.4-1) for the manufacture of parts from Si_3N_4 plasma powder or mixtures with 50% plasma powder and SN-E10 powder.

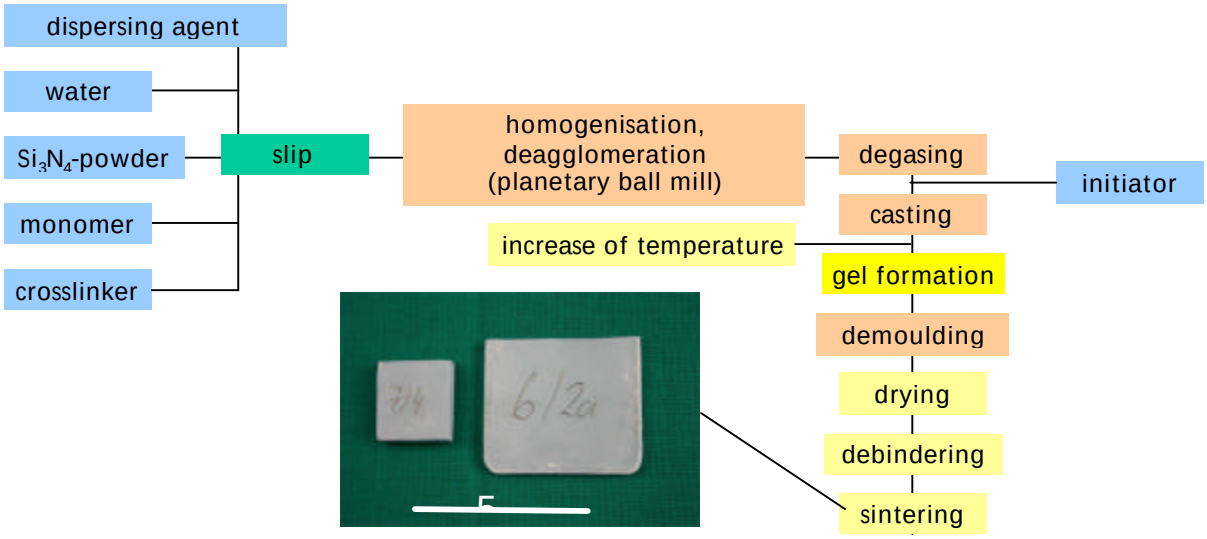


Fig. 2.4-1: gelcasting procedure

The main parameters which had to optimize and their complex influence on the material properties are shown in table 2.3-1.

Table 2.4-1: Development of the gelcasting process

optimized parameters	**influence on**
concentration of monomer and crosslinker	slip viscosity, green strength, drying
solid content of the slip	slip viscosity, green density
ball milling conditions	deagglomeration, particle size distribution
conditions of polymerisation (initiator concentration, temperature)	green compact properties (strength, drying defects)

The plates manufactured by gelcasting were free of defects. This is also expressed in a high level of mechanical properties for parts shaped by gelcasting. The same level of bending strength, hardness and fracture toughness was reached with materials using pure plasma powder shaped by gelcasting. In fig. 2.4-2 the bending strength of parts shaped by gelcasting, MPIM and CIP was compared.

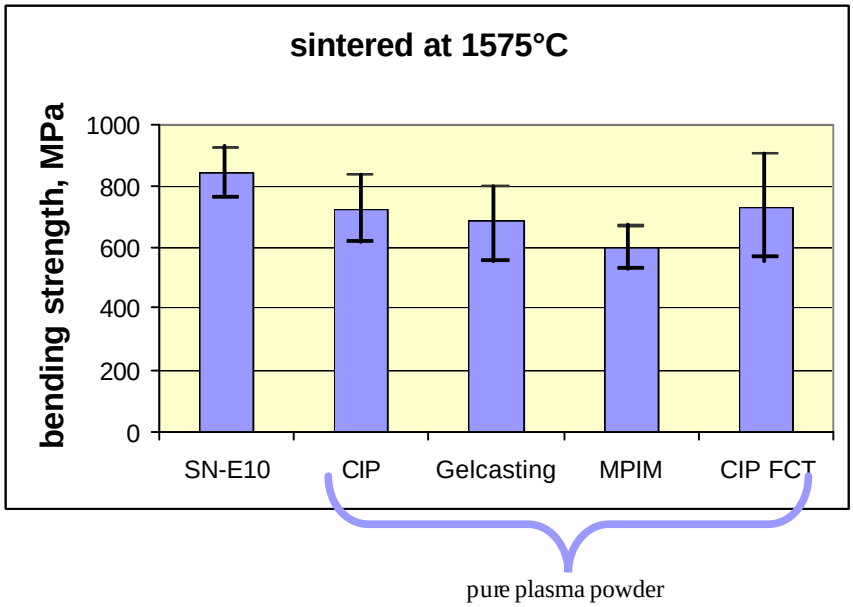


Fig. 2.4-2: Comparison of bending strength from materials shaped by CIP, gelcasting and MPIM using SN-E10 or pure plasma powder compositions

MPIM /PIM of nano Si_3N_4 composite powder

Beside a material using pure plasma powder also a mixture with 50% plasma powder and SN-E10 powder were used during the project in different technological routes. Based on the good mouldable feedstock (M3) IKTS developed the MPIM technology for the equipment leased from Goceram. The running-in was conducted with test bars and rings. A workshop about the MPIM technology took place together with Formatec on the CERAMITEC 2006. MPIM technology can bring benefits. In the future Formatec expects benefits in the homogeneous mould filling for parts with big differences in wall thickness if they use the MPIM technology.
Materials produced by MPIM using pure plasma powder possess an only slightly lower bending strength than CIPed one (Fig.2.4-2). Their hardness, fracture toughness and microstructure are comparable with CIPed materials (table 2.5-2).

Spray granulation of ZrO_2 powder

Additional RTU performed activities to improve the spray-drying equipment, to determine the suspensions suitable for spray-drying and to optimize the spray-drying parameters.
In the result they delivered the following spray granulates using the plasma processed zirconia powder grade B:

Tabel 2.4-2: Overview about the delivered spray granulate batches from zirconia grade B

Charge No	amount, kg	reCIPient / user	delivering date
ZrO2-Y-Al-5/37-45/165-168 G	0,77	Formatec	November 2005
ZrO2-Y-Al-5/37-45/165-168 F	0,62		
ZrO2-Y-Al-5/41;52/175-177 G	0,90	TKC	January 2006
ZrO2-Y-Al-5/41;52/175-177 F	0,90		

The apparent bulk density could be incresed from 0.25 (as plasma processed) to 1.57g/cm^3 after spray granulation. The spray granulate was shaped by CIP at 100MPa and sintered by TKC (see chapter 2.5).

Freeze granulation of ZrO_2 powder

Freeze granulation was conducted with 7.5 vol% PVA/PEG as pressing aids.
Each 2kg TZ-3Y-E and TZ-3Y-20A powder was freeze granulated by IVF for investigation the sinterability and testing by TKC. The freeze granulate was also uniaxial pressed at 20 MPa and then CIPed at 300 MPa for sintering in the range 1300-1600ºC and mechanical testing by IVF. For the material from TZ-3Y-E powder a maximal bending strength of 463MPa and from TZ-3Y-20A powder a maximal bending strength of 716MPa were measured by IVF. But in the materials from freeze granulate agglomerates as strength limiting factor were detected. A fine tuning of the processing is necessary by extensive milling to de-agglomerate, sieving at 5-10 µm, optimizing the amount of pressing aids and the sintering process. The freeze granulate was shaped by CIP at 100MPa and sintered by TKC. For freeze granulate of the powder TZ-3Y-E full dense parts with a biaxial bending strength of 567MPa could be produced by TKC. The evaluation of the freeze granulate of TZ-3Y-20A take place via sintering and HiP to get a fine microstructure and a high density. The evaluation of the formed microstructure and level of bending strength is still running.

MPIM / LPIM of ZrO_2 powder

With the zirconia powder grade B only insufficient results were reached by Goceram. The feedstock with only 43vol% solid content showed poor sintering performance (≈93% of theoretical density). Due to the quality problems with the plasma zirconia powder IVF and Goceram went on with the use of partially stabilized zirconia powder TZ-3Y-E and TZ-3Y-20A delivered by Tosoh. They developed a homogeneous feedstock with a solid content of 46vol% which could be processed by MPIM with a good quality.
TKC developed in parallel feedstocks for LPIM using 4 zirconia powders of Tosoh. TKC reached solid contents between 42.8 and 49.6vol% in dependency on the used zirconia powder. In comparison a solid content of 35vol% could be reached only by TKC using the zirconia powder grade B of PCT (batch: ZrO_2-Y-Al-5/45).
Formatec conducted shaping tests with their PIM (high pressure injection moulding) equipment using ZrO_2 plasma powder grade B. They used the commercially available Licomont TPEK 583 and an own binder system based on polyacetal in the tests. Several mixing trials were preformed with both binder systems to find an acceptable feedstock. With the Licomont binder system a higher solid loading could be reached compared to the binder commonly used by Formatec. Compared to zirconium TZ–3YS the feedstock had to mix longer in the Z-blade mixer to get a homogeneous feedstock .The first injection-moulding test was done in a mould with a runner and a simple cavity (fig. 2.4-3). Because of problems with the filling of the mould a second small part was tested with a short gate directly on top of the part (fig. 2.4-4). But the test was not continued due to the quality problems with the ZrO_2 plasma powder grade B.

Fig. 2.4-3. simple part from zirconia plasma powder shaped by PIM

Fig. 2.4-4: Second part from zirconia plasma powder shaped by PIM

Deliverables / Milestones

D17:" Pressing and characterisation of ZrO_2 parts produced by using spray and freeze granulate"

The work so far has shown that it is possible to disperse the nano-ZrO_2 powder Grade B up to about 33vol% effective solids loading by using a PAA/PEG comb polymer (KD7) as dispersant.

All slips were then subjected to freeze granulated/freeze-dried by IVF.

After freeze-drying the granules were be sieved (710µm) and the tap density and flow property was determined with the results presented in Table **2.4-3**. As comparison a commercial ZrO_2 pressing powder (TZ-3YSB, Tosoh) with the same composition as grade B was also characterised.

Table **2.4-3**: Properties of granules after freeze drying

Sample	**Flow[1] (s/50 g)**	**Tap density[2] (g/cm^3)**
A	103.0	1.25
B	117.0	1.13
C	90.6	1.28
D	105.5	1.22
TZ-3YSB	68.8	1.21

[1]According to standard SS 11 10 31 for metal powder

[2]According to standard EN 23 923-1 for metal powder

[3]Theoretical densities included organic additives

Overall, the tap density was considered satisfying for a production case whereas the flow properties might be improved to fulfil the requirement for an automatic pressing process.

The granules achieved by freeze granulation possess a spherical shape and a wide size distribution

The first batch of the spray dried nano zirconia was mainly used by Diceram to investigate the compacting and subsequent machining behaviour by turning and milling. Geometry of the green bodies and pressures used in the CIP has been chosen similar to the specimen used in the manufacturing of endoscopes tips. Machining of the green bodies was possible although cutting speeds were lower compared to the TOSOH spray dried powders. The density of the sintered ceramic was lower than those obtained with the conventional powders. Microstructure and grain size of the ceramics have been examined for the sintered and the HIP samples (**Fig.2.4-1**). The average grain size for the ceramics from nano ZrO_2 was roughly

2/3 of the grain size of samples made with the conventional powders. To reduce the grain growth the presence of bigger particles in the starting powders should be reduced. In addition the microstructure showed some cracks, which were reduced in size but not eliminated if the samples undergo a subsequent HIP treatment (**Fig.2.4-2**).

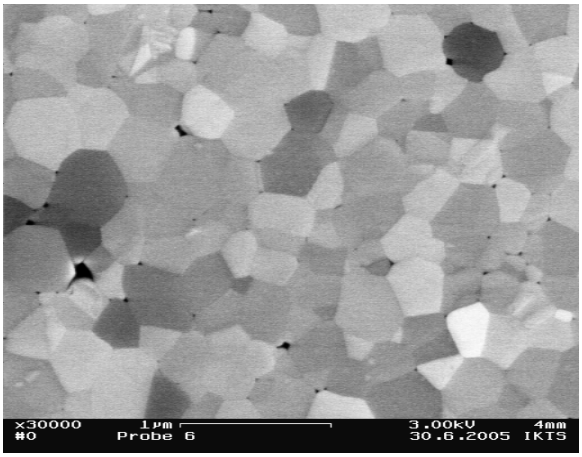


Fig. **2.4-1**: Microstructure of HIPed samples manufactured by Diceram using nano ZrO_2 powder

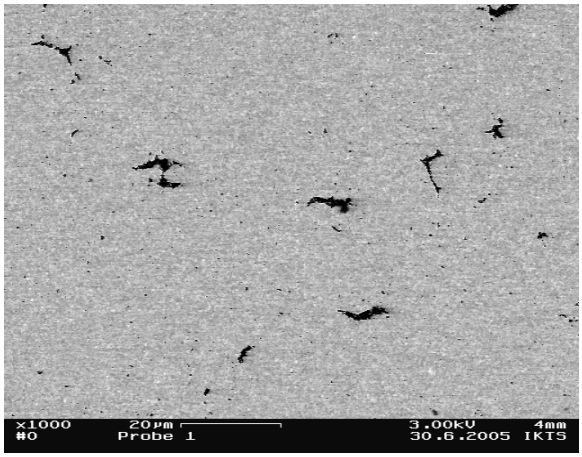


Fig. **2.4-2**: Cracks in samples manufactured by Diceram using nano ZrO_2 powder

D19: "PIM equipment and technology for Si_3N_4"

By medium pressure injection moulding samples (test bars and rings) were manufactured and characterized. Debinding technology was improved and it was shown, that carbon free debinding is possible. Finally a solid content of 76.0 wt % was achieved. The prepared feedstock was used for the production of parts in the new MPIM equipment (medium pressure injection moulding), supplied by Goceram.

D20: "Shaping experiments of ZrO2 test bars by MPIM"

Various shapes were made by GOCERAM with the same moulding parameters, including parts of various wall thickness (1 mm – 10 mm) and shape complexity.

D29: "Shaping experiments for cylindrical green bodies and test bars by gel casting of Si_3N_4"

Plates and test bars were shaped by gelcasting technology from pure plasma powder and mixtures of 50% plasma powder with SN-E10. These bodies were used for the measurement of bending strength after cutting and grinding. The reached level of mechanical properties is nearly the same as the level of CIPed samples (see tab.2.5-2).

D35:" Development of drying procedure, characterisation of green compacts made by gel casting"

The drying procedure has a strong influence on the quality of green and sintered bodies. A drying with too high heating rates causes cracks and big pores in the body due to shrinkage of the polymer can not take place in time at the selected temperature. Therefore tests were conducted to dry in a climatic chamber under defined humidity. The results showed no differences in the quality of green and sintered bodies in comparison to the drying procedure in air. The following tests were done with drying procedures in air but with a defined temperature range. The drying is necessary up to residual moisture of maximum 4wt%.

D41:" Optimised shaping and drying procedure for gel casting of Si_3N_4"
In result of the development an optimised shaping and drying procedure was provided. Based on these sintered bodies could be produced by gelcasting which possess the same level of bending strength, fracture toughness and hardness as CIPed samples (fig.2.4-2, tab.2.5-2)

D36: "Shaping experiments of Si_3N_4 test bars by MPIM"
The shaping experiments with Si_3N_4 test bars were successful. In the results sintered test bars could be manufactured which possess only slightly lower bending strength than CIPed one (Fig.2.4-2).

D37:" Shaping of Si_3N_4 prototypes by MPIM and mould construction"
The mould (fig.2.4-5) were constructed and built to produce saw teeth for wood working by MPIM. The shrinkage of the saw teeth during sintering was determined by help of injection moulding of test bars 5.5 mm x 6 mm x 70 mm. with 19.65%. Based on this shrinkage the mould was constructed.

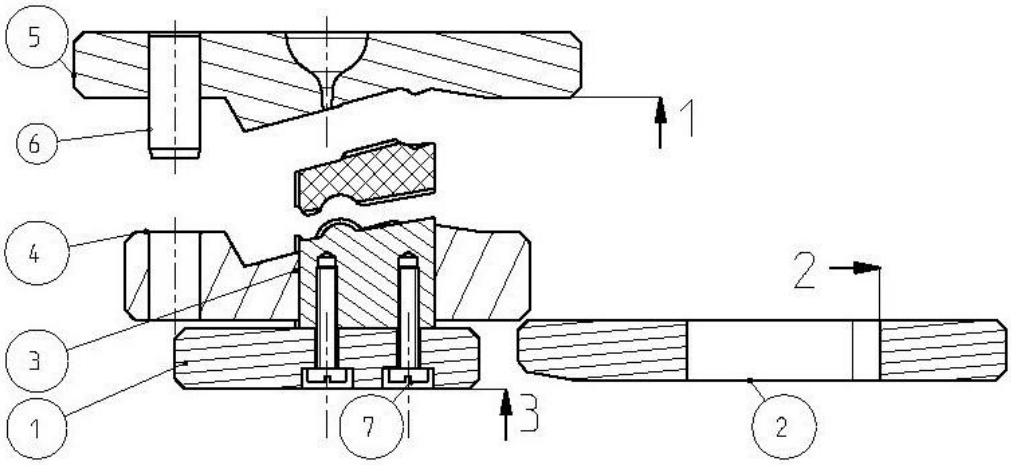


Fig. 2.4-5: Mould of the saw teeth, which was used for MPIM

D42:" Characterisation of Si_3N_4 parts produced by MPIM"
The Si_3N_4 parts produced by MPIM were characterised by the sintering density, content of pores at the surface of a polished sample, bending strength, fracture toughness and hardness. Very dense parts with low porosity could be produced by MPIM technology (tab. 2.5-2).
Materials produced by MPIM using pure plasma powder possess an only slightly lower bending strength than CIPed one. Their hardness, fracture toughness and microstructure are comparable with CIPed materials. From the feedstock Craft4 using a mixture with SN-E10 dense parts could be manufactured. I opposite the feedstock Craft5 using the same mixture with SN-E10 was not optimal. The samples showed an enhanced porosity with big pores. From this reason the reached level of bending strength was lower in comparison the level of CIPed samples.

D43:" Preparation of a optimised granulate of ZrO_2"
Spray granulate of ZrO_2
The technology of spray drying was optimised for the own spray drying equipment by RTU. The first assumption was an improvement of the spray-drying equipment in order to guaranty the process stability according to requirements of quality management norms of EN ISO 9001:2000. The new temperature control and measuring systems are built in the spray-drying apparatus. The performed improvements of spray-drying technological equipment ensure:

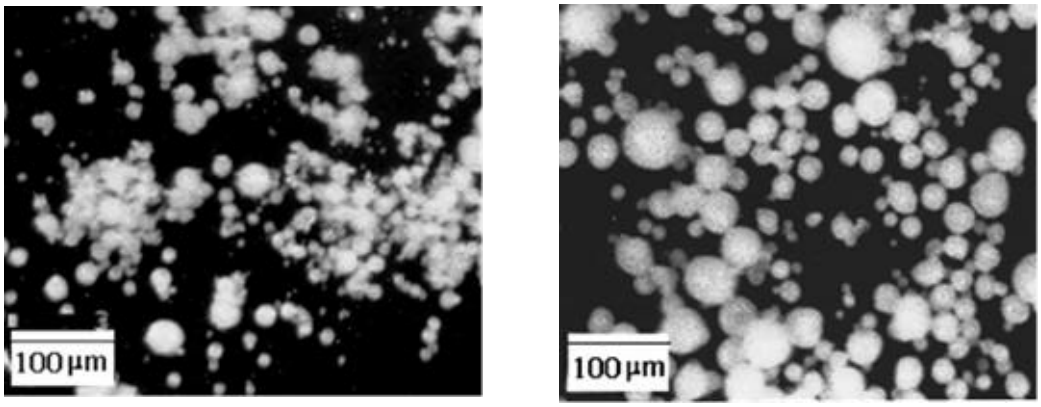
- Keeping constant air flow rate independent on filter resistivity during drying process;
- Automatic hot air temperature regulation independent on air flow rate with accuracy of ± 2 ^{0}C;
- Temperature control in evaporation chamber with accuracy of ± 1 ^{0}C.

The following process parameters were found to deliver well adapted spray granulates from zirconia plasma powder grade B and a high product yield:

Tab.2.4-3: Optimized spray-drying parameters

Parameter	**Optimized value**
Hot air temperature, ^{o}C	370± 2
Hot air flow rate, m^3/h	24
Temperature in evaporation chamber, ^{o}C	115-120
Suspension concentration, wt. %	50-52
Surfactant	KD 7
Content of surfactant, wt. % in relation to powder	3

Both products from the filter and evaporation champer are characterized by a spherical form (Fig. 2.4-6). The product obtained from filter is finest with tend to made agglomerates.



a **b**

Fig. 2.4-6: Product from filter (a); Product from evaporation chamber (b)

The granulated powders possess an up to six times higher bulk density compared to plasma synthesized powder. Apparent and tapped bulk densities are practically close for both products obtained from filter and from chamber.

Table 2.4-4: Characteristics of granulated powders - bulk density

Powder	Bulk density, g/cm^3	
	apparent	tapped
As plasma-processed	0,25	0,40
Granulate from filter	1,57	1,64
Granulate from chamber	1,56	1,61

Freeze granulate of ZrO_2

In the first year investigations were conducted by IVF developing optimal freeze granulates based on the plasma powder grade B. The following images with varied magnifications show cross sections of the freeze granules. These structures contain nano particles. However, in the granules also a frequent number of larger grains (typically 1-5 µm) appear as lighter (dense) particles. We can assume that these are the larger particles detected in the investigation of the as-received powder.

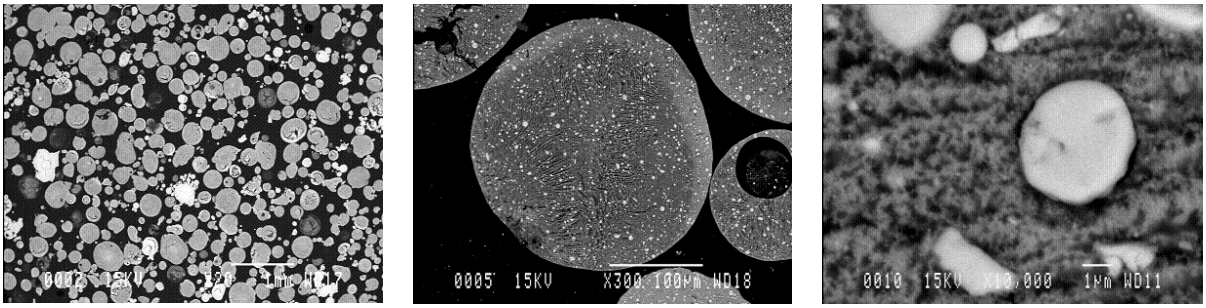


Fig. 2.4-7.**:** Cross sections of granules based on plasma powder grade B, batch 4/42 at varied magnifications

Owing to the presence of coarse particles in the nanopowder batches it was decided to produce granules and materials based on alternative ZrO_2 powders, e g Tosoh TZ-3Y-E (?=6.05 g/cm^3) and TZ-3Y20A (?=5.50 g/cm^3).
Larger batches (ca 2 kg powder) were prepared for granule delivery to TKC by 48 hours ball milling, 2.5 resp 3.5 kg balls in a gallon container using the reCIPes in tab. 2.4-5.

Tab. 2.4-5 : Slip compositions with Tosoh powder for freeze granulation

Material (g)	TZ-3Y-E (1)	TZ-3Y20A (2)
Powder	2117.5	2310
Dispersant (25%)	50.18	55.4
Distilled water	599.2	724.56
Slip volume (ml)	1000	1200

Freeze granulation took place with 6 l/h and 0.35 bar air pressure for the smaller as well as for the larger slips prepared. The output for the larger batches was after freeze-drying 1886 g of 1 and 2019 g < 710 µm for material 2. The total amount of organic used was 2.0 for powder 1 and 1.9 wt% for powder 2. These granule batches were sent to TKC for pressing of components, sintering and material evaluation.
The following images show the cross section of granules from Tosoh powder with essential spherical shape. At higher magnification structures can be seen caused by ice crystal growth in the in-freezing step. This phenomenon is not considered to cause any serious negative effect on the granule properties. More serious is the appearance of larger (lighter) particles within a matrix of nano particles with a size in the range of 2-10µm, often with an elongated shape. They consist of zirconia and are denser than the surrounding. This indicates that they are tight agglomerates, probably present in the as-received powder and not properly de-agglomerated by the milling procedure.

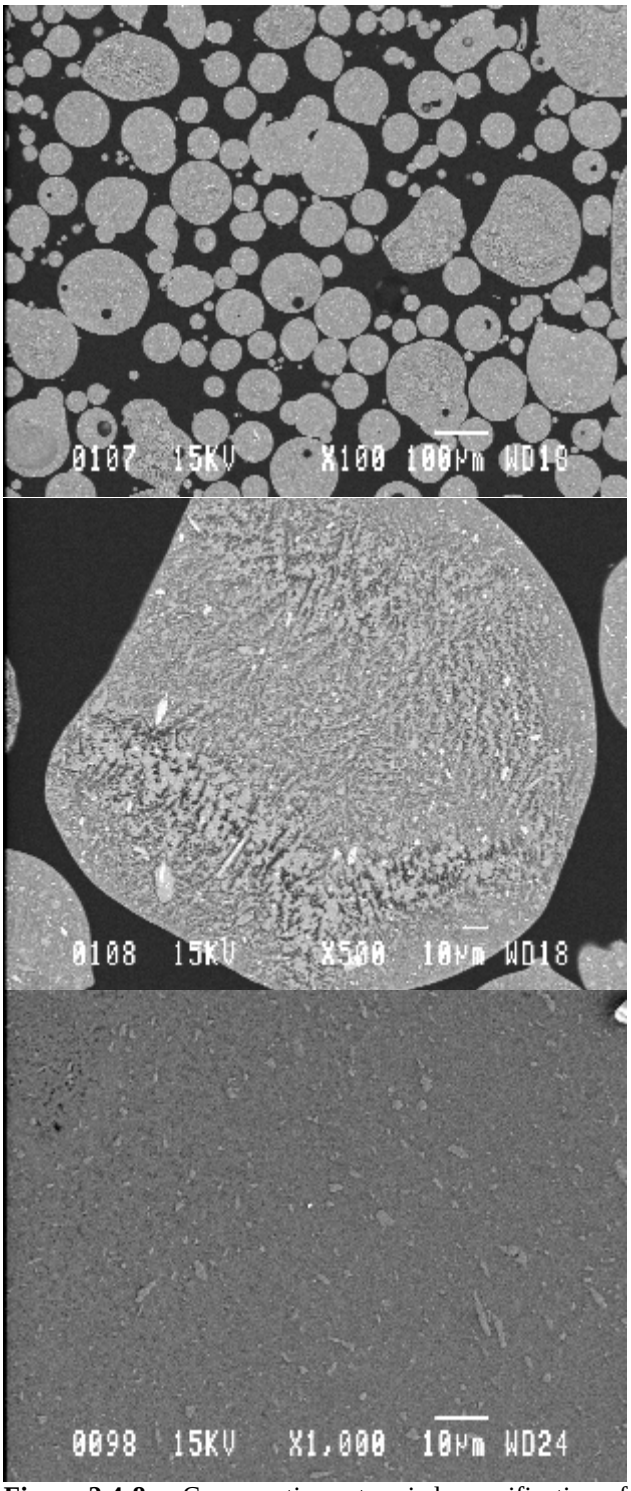


Figure 2.4-8 a: Cross sections at varied magnification of debinded granules based on TZ-3Y-E

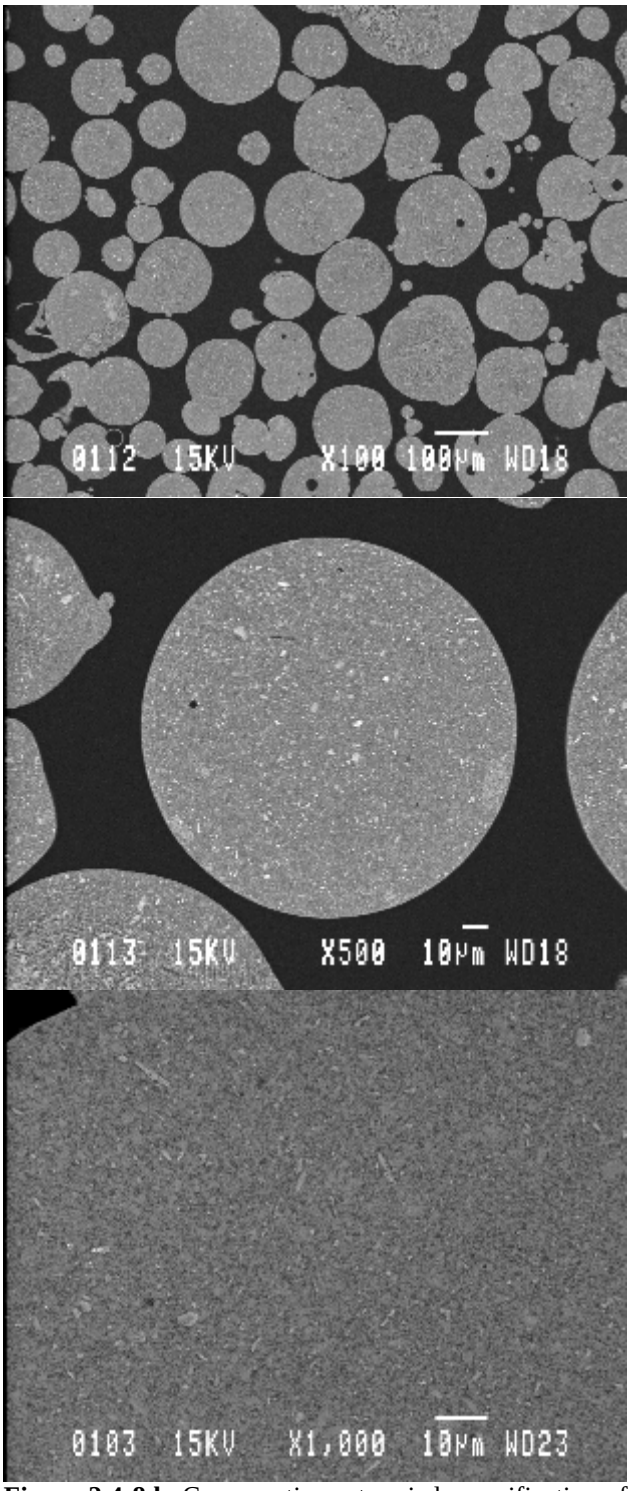


Figure 2.4-8 b: Cross sections at varied magnification of debinded granules based on TZ-3Y20A

The granules prepared for internal use were sieved to 45-710 µm and characterised regarding flow and tap density with the following results:

Table 2.4-6: Properties of the two granule batches

Powder	Flow[1] (s/50 g)	Tap density (g/cm^3)	Tap density (% of theor)
TZ-3Y-E	118.1	1.04	18.8
TZ-3Y20A	149.9	0.88	17.5
plasma powder grade B, batch 1	103.0	1.25	25.2
plasma powder grade B, batch 2	117.0	1.13	23.6
plasma powder grade B, batch 3	90.6	1.28	25.8
plasma powder grade B, batch 4	105.5	1.22	25.7

[1]According to standard SS 11 10 31 for metal powder

[2]According to standard EN 23 923-1 for metal powder

[3]Theoretical densities included organic additives

The granule properties obtained with Tosoh powder were less good than with Grade B. It can be many factors responsible for this such as the amount of organic additives and differences in granule size distribution.

D44:" Characterisation of ZrO_2 parts produced by MPIM"

The development of ZrO2 parts produced by MPIM using zirconia plasma powder was not continued due to problems with the quality of the powder. As for pressing it was decided to use the Tosoh powders TZ-3Y-E and TZ-3Y20A as alternatives for Grade B within the project.

Powders were pre-treated by IVF in a similar manner as done with Grade B. However, in this case it was not possible to conduct preparation of slips based on cyclohexane without stearic acid. The slips became heavily aggregated but small additions (0.4 wt%) of stearic acid turned the situation into a homogenous slip state, possible to process by freeze-granulation. Again, as already shown in water processing, the Tosoh ZrO_2 display different surface chemistry and behaviour in liquid medium compared to Grade B.

With a special binder system GOCERAM developed a moldable homogeneous feedstock for MPIM. The solid content of the mouldable feedstock was 46vol%- Both Tosoh powders reached in general 5 – 7 % higher solids content compared to the PCT powders despite comparable BET specific surface areas. The parts produced by MPIM can be sintered full dense.

2.5 Binder burning out / sintering – workpackage 5

Participant involved	IKTS	IVF	FORMATEC	FCT

Objectives

- Technology development of the binder burning out and sintering for the production of prototypes from Si_3N_4 and ZrO_2 using nanosized powders taking the selected shaping methods into consideration
- Evaluation of the microstructure and materials properties in relation to demands in the designed application field

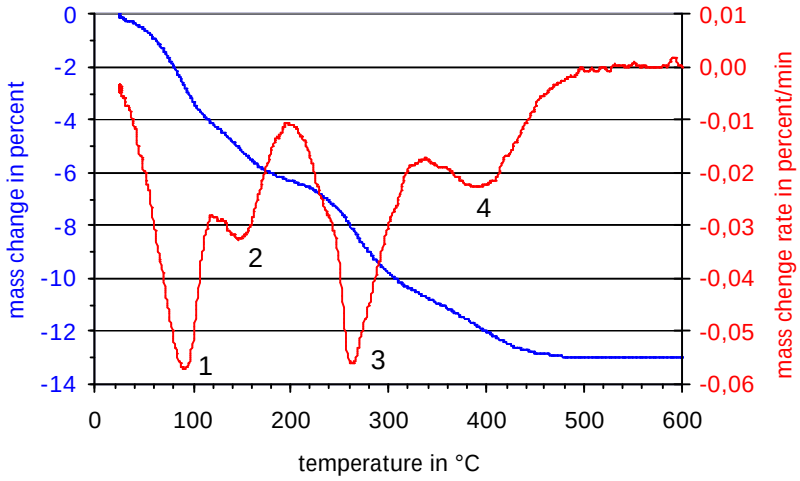
Progress

Nano Si_3N_4

Parts shaped by CIP, MPIM and gelcasting using pure plasma powder or mixtures from 50% plasma powder and SN-E10 were sintered by IKTS. Therefore optimised binder burning out and sintering regimes had to develop. The removal of pressing aids from CIPed parts took place in air after a special regime over 14h without an unrequested increase of oxygen content in the material.
Due to the higher binder content in parts after gelcasting and injection moulding the binder burning out regimes is a critical process step in the technology which determined the quality of the sintered parts. The gelcasting green compacts were investigated concerning their debindering behaviour. All organic additives (the formed polymer, dispersing agent) are removed until 450°C during heating under air. A thermogravimetric curve is presented in figure **2.5-1.** Before debindering the drying is necessary up to residual moisture of maximum 4wt%.

Figure **2.5-1**:
Thermogravimetric curves of gelcast green compact; macro thermo-balance; initial weight: 16,34 g heating rate: 1 K/min atmosphere: 35 l/h synthetic air

1: residual water
2: dispersing agent
3 + 4: polymer and crosslinking agent



Debindering of parts shaped by MPIM was processed under air up to 600 °C. After debindering a carbon content of less then 0.02 wt% was estimated. That means that all binder was practically eliminated during thermal debindering.
After debindering the sintering took place. The used temperature regimes are adapted at the used furnaces. Parts shaped by CIP, MPIM and gelcasting could be sintered after the same regime getting dense parts free of defects and cracks. The sintered samples were evaluated by their density, porosity and mass loss during sintering. The density of the different batches and shaping methods can differ due to changes in the content of oxygen. Therefore the percentages of pore area at the surface of the polished sample had to measure. Only in two

cases a pore content >0.1% was measured. The gelcasting sample GC2-2 processed at an early stage of the project showed big pores caused by a non optimised casting procedure (fig. 2.5-2). The MPIM test bars from the batch Craft5 (fig. 2.5-3) possess a high portion of pores too. In this case there were problems during the feedstock preparation. The feedstock Craft5 has to use for the production of the saw teeth. It was not possible to repeat the manufacture of the feedstock within the project due to the lack of time.

Tab.2.5-1: Results of gas pressure sintering at 1575°C

powder	batch	shaping	sintering	Mass loss, wt%	density, g/cm3	Content of pores, %
100% SN-E10	165	CIP	040605-1	0,15	3,229	
100% SN-E10	165	CIP	061505-1	0,18	3,232	
100% SM128Z	166	CIP	040605-2	0,61	3,224	
50% SM128Z	167	CIP	040605-3	0,50	3,220	0,04±0,02
50% SM130Z	169	CIP	102005-1	0,32	3,258	0,01±0,02
50% SM131Z	170	CIP	102005-2	0,28	3,225	0,01±0,008
50% SM130Z	169a	CIP	022406-1	0,22	3,231	
50% SM130Z	169a	CIP	022406-2	0,24	3,231	
50% SM128F	171	CIP	022406-3	0,29	3,233	
100% SM128Z	GC2-2	GC	053105	0,80	3,223	0,20±0,06
100% SM128Z	Craft3-11	MPIM	053105	0,95	3,202	0,03±0,01
100% SM128Z	Craft3-12	MPIM	053105	0,90	3,201	
50% SM130Z	GC17-1	GC	022406	0,59	3,228	0,03±0,01
50% SM130Z	Craft4 GA-15	MPIM	022406	1,20	3,213	0,06±0,02
50% SM130Z	Craft5	MPIM	071106-1..12	0,82	3,201	0,38±0,12
50% SM130Z	GC21	GC	071106-63/64	0,75	3,223	

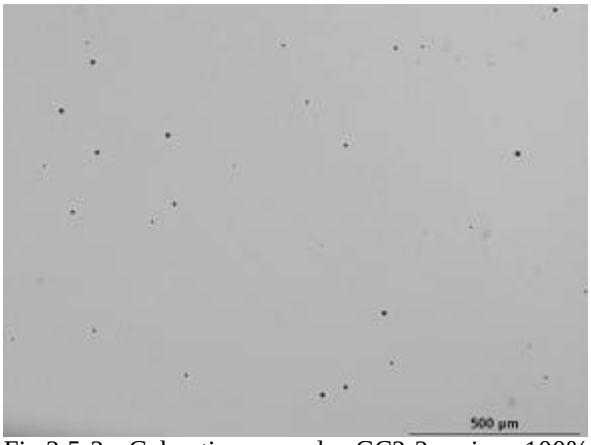


Fig.2.5-2: Gelcasting sample GC2-2 using 100% SM128 with big pores caused by air inclusions during casting
density: 3.223g/cm3
pores: 0.20±0.06%

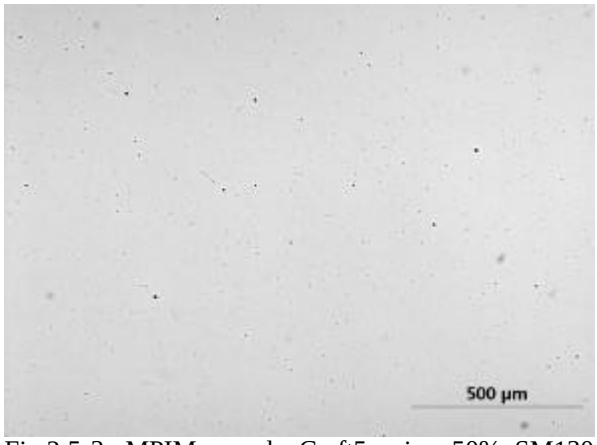


Fig.2.5-3: MPIM sample Craft5 using 50% SM130 with a high porosity caused by a bad feedstock quality
density: 3.201g/cm3
pores: 0.38±0.12%

The sintering temperature was relatively low for the formation of dense materials with nanostructured microstructure (fig. 2.5-4). The sintering took place independent on the shaping method after the same regime.
The bending strength of the nanostructured parts was independent on the shaping method at the same level if the parts are full dense (fig. 2.5-5, 2.5-6). Parts from the feedstock Craft5 using the powder SM130Z were not full dense and showed only a bending strength of 472MPa.

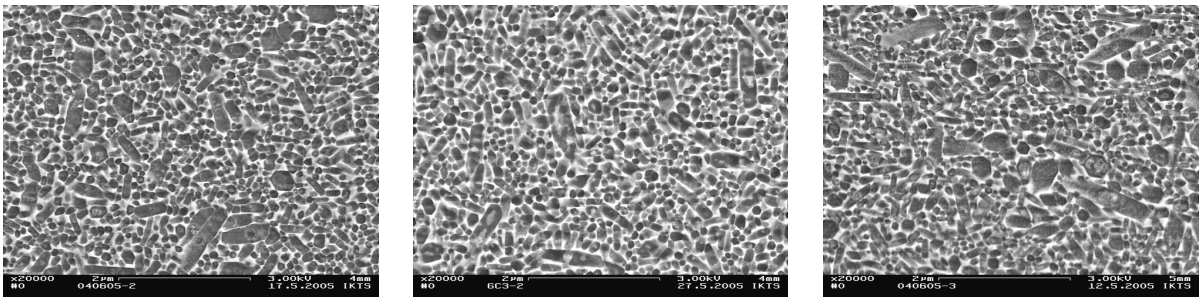


Fig. 2.5-4:Gas pressure sintered materials

a) shaped by CIP using pure plasma powder

b) shaped by gelcasting using pure plasma powder

c) shaped by CIP using a mixture of 50% plasma powder and SN-E10

Tab.2.5-2: Mechanical properties of the sintered Si_3N_4 materials

powder	batch	Shap-ing	sintering	tempera ture, °C	s_{4P}, MPa	K_{IC}, $MPam^{1/2}$	hardness HV10
100% SN-E10	165	CIP	040605-1	1575	840±77	4,8	1536
100% SN-E10	163	CIP	012605-5	1700	998±84	5,2	1473
100% SM128Z	166	CIP	061505-2	1550		4,3	1596
100% SM128Z	166	CIP	040605-2	1575	724±107	3,8	1484
100% SM128Z	162	CIP	012605-4	1700	731±127	5,3	1443
100% SM128Z	GC2-2	GC	053105	1575	685±131	4,2	1503
100% SM128Z	Craft3-11	MPIM	053105	1575	597±68	3,7	1500
50% SM128Z	167	CIP	040605-3	1575	884±60	4,5	1522
50% SM130Z	169	CIP	102005-1	1575	756±120	3,7	1533
50% SM131Z	170	CIP	102005-2	1575	774±104	3,6	1531
50% SM130Z	GC17-1	GC	022406	1575		4,1	1540
50% SM130Z	Craft4 GA-15	MPIM	022406	1575		4,0	1516
50% SM130Z	Craft5	MPIM	071106-1..12	1575	472±105		
50% SM130Z	GC21	GC	071106-63/64	1575	672±74		

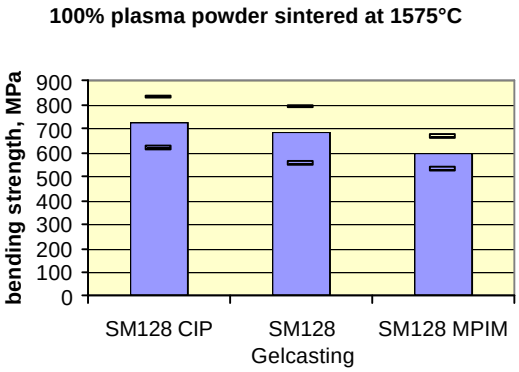


Fig.2.5-5: Comparison of the bending strength level between different shaping methods using 100% plasma powder (batch SM128)

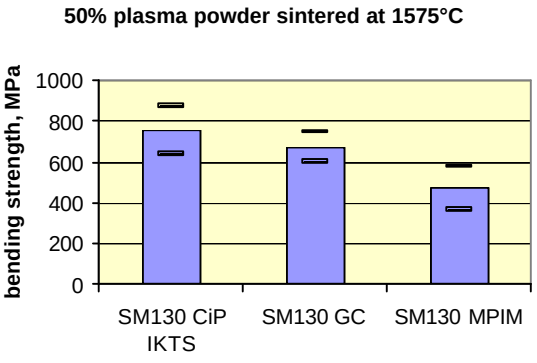


Fig.2.5-6: Comparison of the bending strength level between different shaping methods using 50% plasma powder (batch SM130)

Nano ZrO_2

The removal of pressing aids from CIPed zirconia parts took place in air after a special regime over 14h. In comparison the binder burning out regime is a critical process step in the technology of MPIM and LPIM parts which determines the quality of the sintered parts. If the solid content in the feedstock is to low (lower than 42vol%) then the parts with higher wall

thickness can not be debindered fully and the parts soften plastically and deform. So parts using the plasma powder grade B could not be processed by MPIM. The duration of the debinding process took between 28 and 48h. In the result TKC could produce thin-walled parts (Thickness <4mm) with sintering densities >99% which are applied in the medicine technique.

The sintering of the different zirconia powders shaped by pressing or LPIM technique was conducted after a special regime in air by TKC. Tab 2.5-3 and 2.5-4 show the sintering densities which were reached in dependency on the sintering temperature. Granulates using the finer powder TZ-3YB or TZ-3Y-E could be sintered fully dense at 1450°C instead at 1500°C and the sintered materials possess a finer microstructure than materials from the coarser powders with 7m^2/g surface area. The powder with the higher Al_2O_3 content TZ-3Y-20A can be sintered fully dense only at 1500°C. To get a fine microstructure these powders have to sinter at 1350°C to get closed porosity and then HiPed to get fully dense materials. The parts made from spray granulate ZrO_2-Y-Al-5/41;52/175-177 (manufactured by RTU) could not even densified fully at 1600°C although zirconia grade B with a surface area of 25m^2/g was used. The reason was the bimodal grain size distribution in the raw powder. The microstructure of the sintered bodies is very coarse in comparison to microstructures generated from the freeze granulate of TZ-3Y-E and even granulate TZ-3YSB-E (fig. 2.5-18, 2.5-19, 2.5-20).

Tab. 2.5-3: sintering density and bending strength of parts shaped by LPIM

powder	BET surface of used powder, m^2/g	Feedstock developed by	Sintering temperature, °C	Density, g/cm^3	Biaxial bending strength, MPa
TZ-3YS-E	7	TKC	1500	6,07	931±100
TZ-3YS	7	TKC	1500	6,03	877±192
TZ-3YS-20A	7	TKC	1350	4,72	
			1500	5,47	
TZ-3Y-20A	14	TKC	1350	4,97	
			1500	5,44	

Tab. 2.5-4: sintering density and bending strength of parts shaped by pressing

powder	BET surface of used powder, m^2/g	Kind of granulate	Sintering temperature, °C	Density, g/cm^3	Biaxial bending strength, MPa
TZ-3YSB-E	7	Tosoh	1500	6,06	702
TZ-3YB	14	Tosoh	1450	6,02	888
TZ-3Y-E	14	Freeze granulate of IVF	1450	6,01	567
			1500	5,47	
TZ-3Y-20A	14	Freeze granulate of IVF	1350	4,97	
			1500	5,44	
TZ-3YS-20AB	7	Tosoh	1350	4,71	
			1500	5,44	
ZrO_2-Y-Al-5/41;52/175-177	25	Spray granulate of RTU	1500	5,10	224
			1550	5,14	
			1600	5,24	178

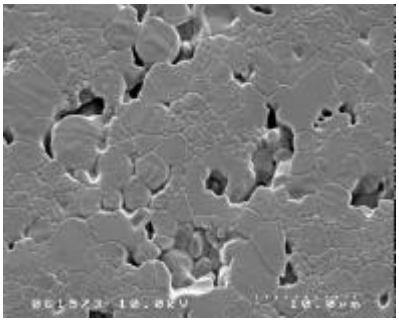


Fig. 2.5-18: Microstructure of material sintered at 1600°C using spray granulate ZrO_2-Y-Al-5/41;52/175-177 of RTU

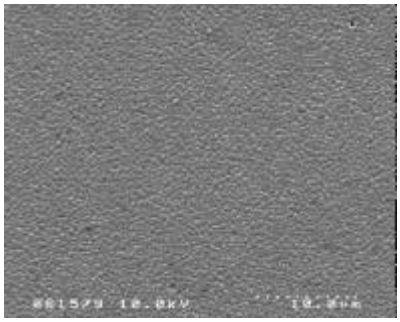


Fig. 2.5-19: Microstructure of material sintered at 1600°C using spray granulate TZ 3YSB-E sintered at 1.500°C

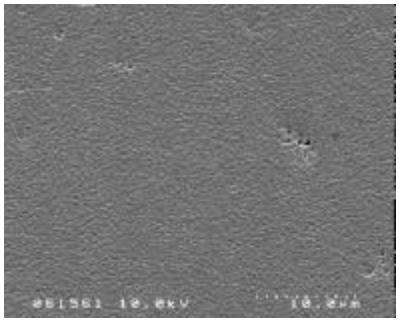


Fig. 2.5-20: Microstructure of material sintered at 1450°C using freeze granulate from powder TZ 3Y-E (generated by IVF)

IVF has also sintered his own freeze granulates from TZ-3Y-E and TZ-3Y20A powder after CIP shaping at 100MPa. From fig. 2.5-7 it appears that the optimal sintering temperature lies in the range of 1350-1450°C for TZ-3Y-E and ca 1550°C for TZ-3Y20A.

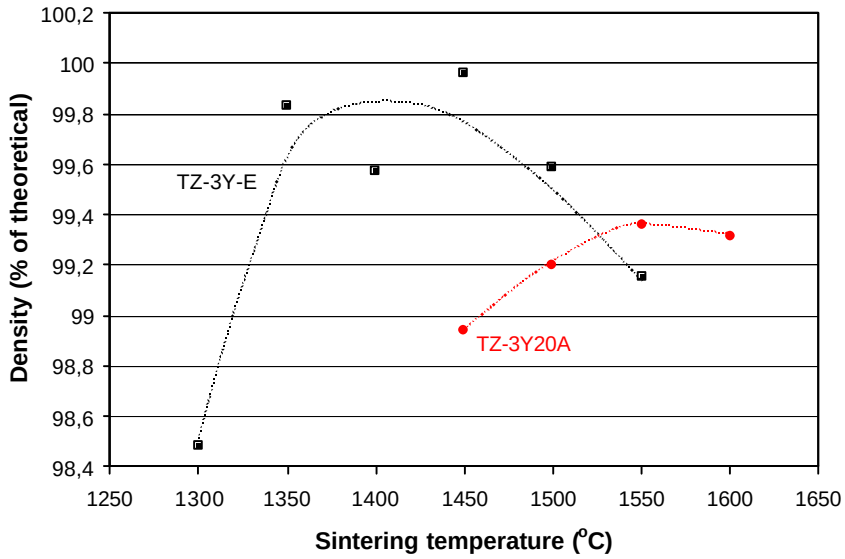


Fig.2.5-7 : Density data for uniaxial pressed and sintered specimens

Table 2.5-5: Results from bending tests of bars based on the various materials produced.

Material	**Sintering temp (°C)**	**4_{pt}-bending (MPa)** Average of 8-10 bars	**Standard deviation**
TZ-3Y-E	1350	463	41
TZ-3Y-E	1450	450	62
TZ-3Y20A	1550	661	65
TZ-3Y20A	1600	716	115

The results obtained with TZ-3Y-E freeze granulated was clearly below the expectations as mechanical performance of pressed materials based on the coarser TZ-3YSB-E spray granulate of Tosoh lies in the range of 700-800MPa. The result with TZ-3Y20A freeze granulated was better but still not on a level that can be expected with a dense nano material. The properties of the materials from TZ-3Y20A can be increased additionally by sintering at a lower sintering temperature (1450°C) and sinter HiP after it. With this technology the microstructure remains finer, the parts become fully dense and the bending strength increases.

The explanation to the moderate mechanical performance using freeze granulate of IVF was indicated by the following SEM investigations.
Figure 2.5-8 shows the microstructure at lower magnification of materials based on TZ-3Y-E sintered at various temperatures. At lower temperatures pores which look like granule defects can be observed. It is less of them in the materials sintered at higher temperatures. At 1500°C a large amount of small spherical shaped pores have been detected which are a possible effect of "over-sintering". The greater porosity in this material was also confirmed by the density measurement.

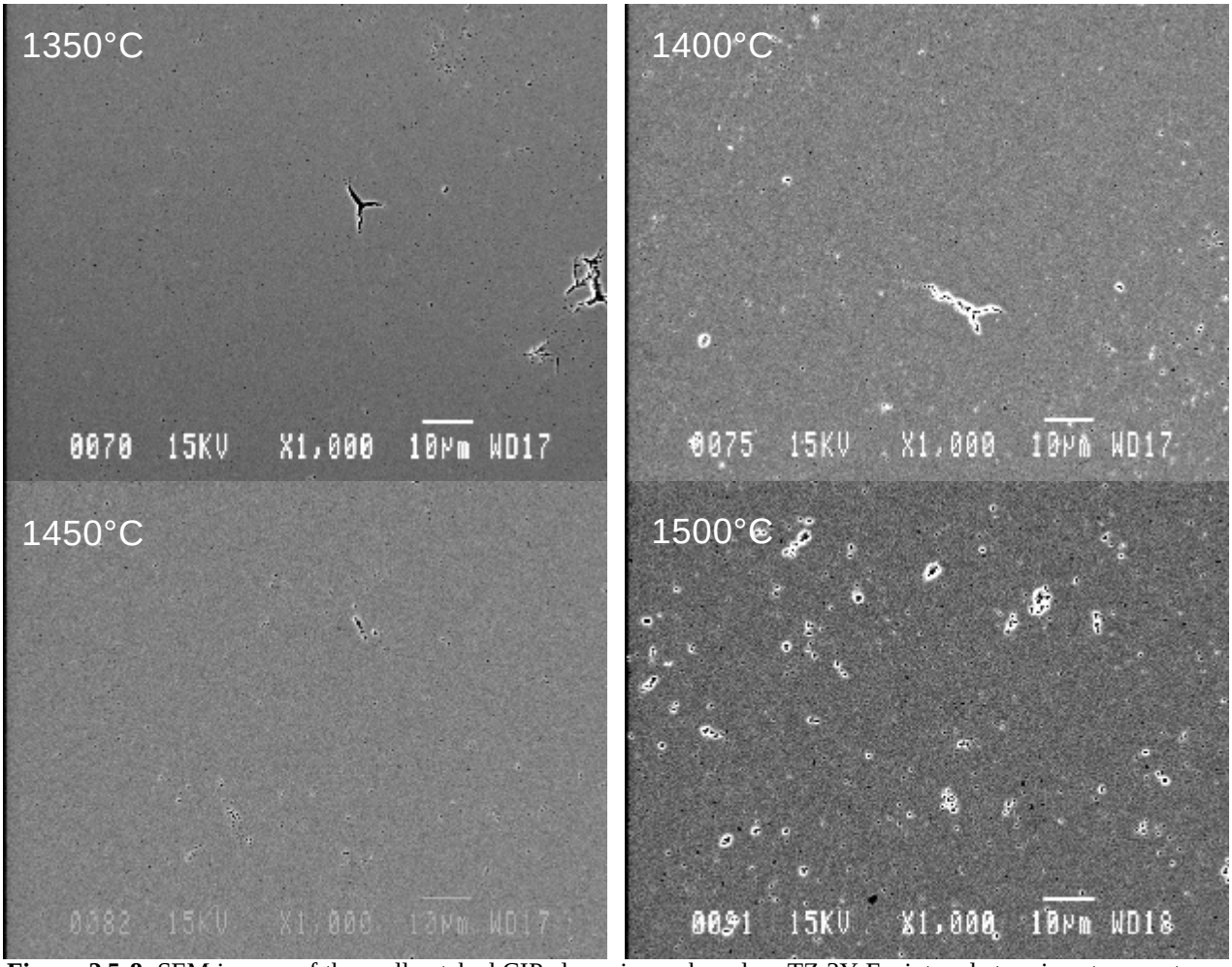


Figure 2.5-8: SEM images of thermally etched CIPed specimens based on TZ-3Y-E, sintered at various temperatures

At higher magnification the development of the grain structure can be detected as illustrated in Figure 2.5-9.

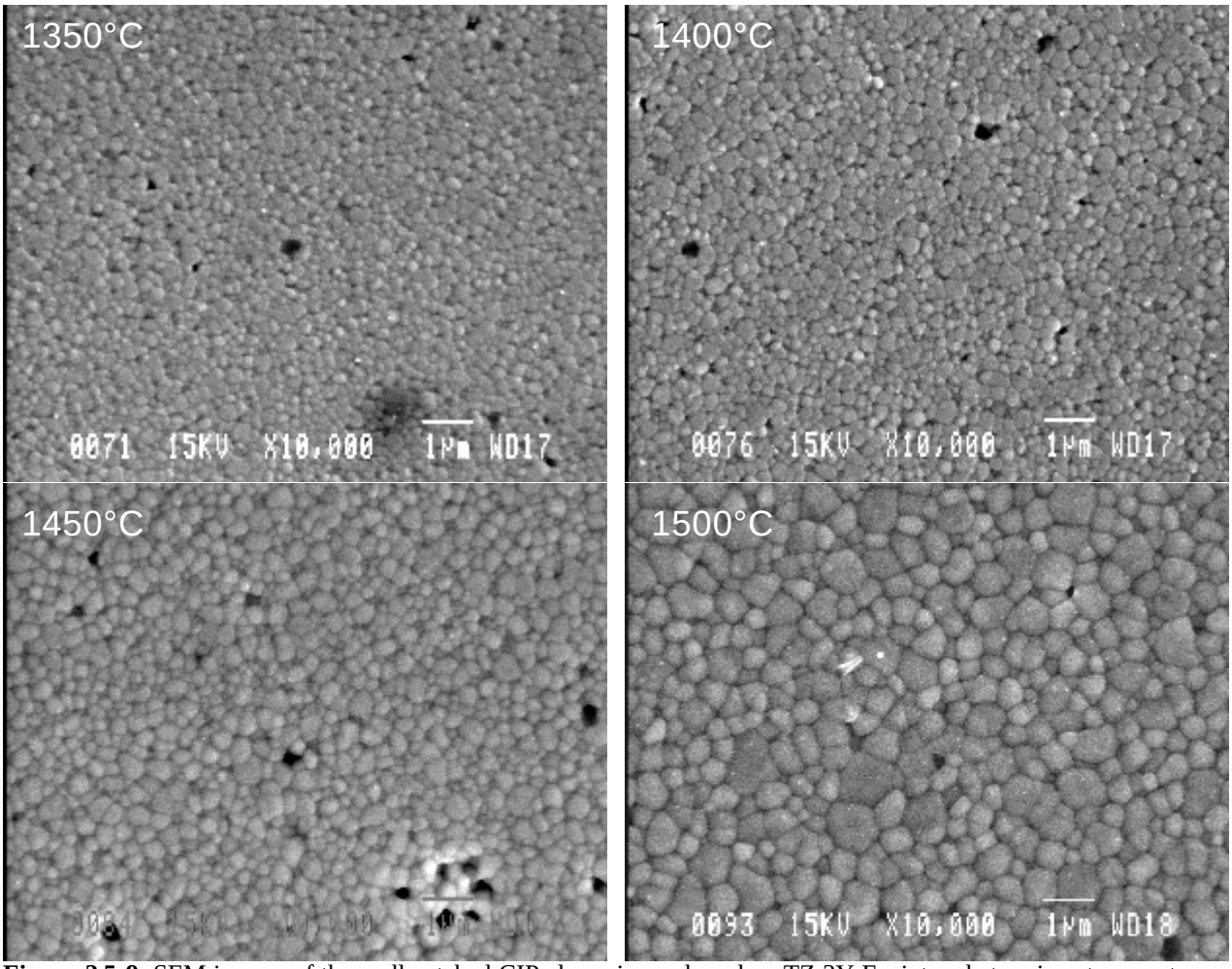
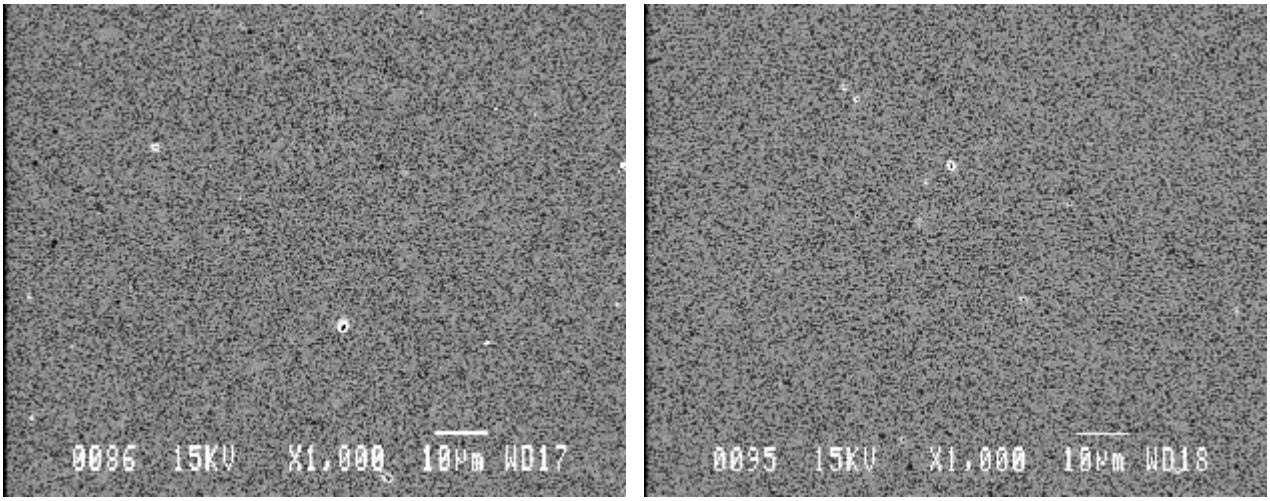


Figure 2.5-9: SEM images of thermally etched CIPed specimens based on TZ-3Y-E, sintered at various temperatures.

In general the materials from the powder TZ-3Y-E are dense and homogeneous with only a few very small pores, however, sometimes in clusters. The effect of sintering temperature is clearly displayed by the grain coarsening (fig.2.5-9).



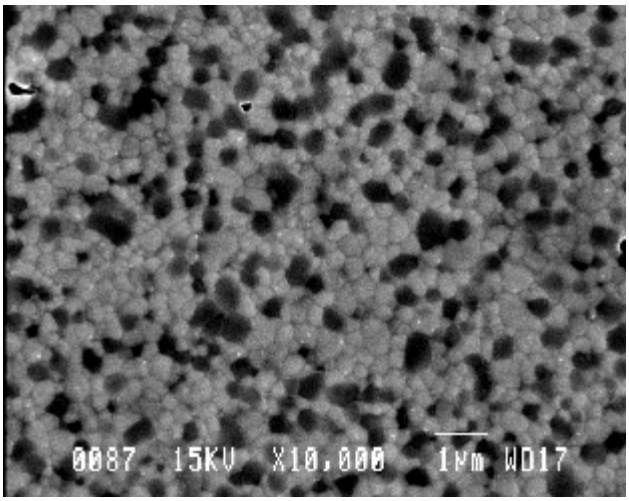


Figure 2.5-10 a: SEM images of thermally etched CIPed specimen based on TZ-3Y20A, sintered at 1500°C.

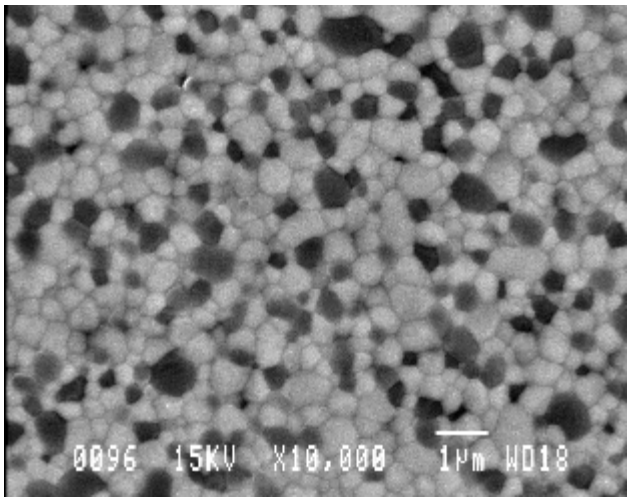


Figure 2.5-10 b: SEM images of thermally etched CIPed specimen based on TZ-3Y20A, sintered at 1550°C.

In the materials using powder TZ-3Y20A powder (fig. 2.5-10), no granule-derived pores was detected, only a few small spherical shaped pores. The grain structure appeared homogeneous with well distributed alumina grains (dark) among a matrix of zirconia grains of similar size. The effect of sintering temperature is also here displayed by a coarsening of grain structure with higher temperature, i e can be expected to continue further in the materials sintered at 1600°C. An improvement of the mechanical performance can be expected for materials using TZ-3Y20A by the application of a sintering at 1350°C and HiPing. However, strongly suspected is the agglomerates detected both in granules and pressed specimens. Even though they are rather small (<20 µm) they can appear, more or less, close to each other and form larger strength-limiting defects in the material.
In order to optimise the processing and avoid the presence of agglomerates in freeze-granulated nano-powders the following is proposed:

- Slip preparation at lower solids loading (lower viscosity), possibly with addition of alcohol as the diluting medium.
- Extensive milling to brake down the agglomerates as complete as possible.
- Sieving at 5-10 µm prior to addition of pressing aids.
- Possible evaporation of alcohol to increase the solids loading prior to freeze granulation in order to achieve higher granule density.

The results basically show that the overall best option is to integrate freeze granulation with the powder manufacture. This will minimize the risk for hard agglomerates and fully utilization of the advantages of this granulation technique.

Deliverables /Milestones

D24: "Thermal analysis of injection molded Si_3N_4 parts"
The debinding technology was improved by IKTS and it was shown, that carbon free debinding is possible.

D25:"Debinding procedure for injection moulded ZrO_2 parts"
Only insufficient densities were reached for injection moulded parts using the zirconia grade B. The reason was the quality of the powder and not the debinding procedure as assumed at first. No problems existed in the quality of injection moulded parts after sintering if the powder TZ3Y-E and TZ3Y-20A was used.

D38:" Debindering procedure for injection moulded Si_3N_4 parts"

Debindering of parts shaped by MPIM was processed under air up to 600 °C. After debindering a carbon content of less then 0.02 wt% was estimated.

That means that all binder was practically eliminated during thermal debinding. All parts produced by MPIM were thermal treated after the same procedure.

D46:" Sintered Si_3N_4 prototypes based on nano Si_3N_4"

The testing in the woodworking industry took place in different companies which are customer of the partner Eberhard, Diamonde or Peitz. Therefore different geometries of the tools from nano Si_3N_4 were necessary. We had to produce sintered plates which were cutted after sintering to get ceramic inserts 3x3x10mm and 10x20x5mm. For milling cutter whole from ceramic we had to sinter rods Ø15mm with length 100mm. These rods were used after finishing as milling cutters or were additional jointed with a metallic shank by shrinkage. Additional saw teeth were shaped by MPIM technology and after binder burning out sintered. The following ceramic parts were sintered from a mixture of 50% plasma powder and SN-E10 for the production of prototypes:

Tab. 2.5-6: Owerview about the sintered prototypes from nano Si_3N_4

prototype	batch	powder	shaping	sintering	Density, g/cm^3	Open porosity, %	Content of pores, %
Ceramic inserts 3x3x10mm	169	50% SM130Z	CIP	102005-1	3,258	0,02	0,01±0,02
Ceramic inserts 10x20x5mm	171	50% SM128F	CIP	022406-3	3,233	0,03	
Milling cutter	169a	50% SM130Z	CIP	022406-1	3.231	0,03	
	169a	50% SM130Z	CIP	022406-2	3.231	0,03	
	169a	50% SM130Z	CIP	GDS_010906 -1	3.215	0,03	
	169a	50% SM130Z		GDS_122005 -1	3.222	0,00	
	169a	50% SM130Z		GDS_122005 -2	3.223	0,03	
Milling cutter joined with metallic shanks by shrinkage	169a	50% SM130Z	CIP	GDS_010906 -1	3.215	0,03	
	169a	50% SM130Z	CIP	GDS_010906 -2	3,215	0,00	
Saw teeth	Craft5	50% SM130Z	MPIM	071106	3,201	0,10	0,47±0,24

The absolute values of density after sintering can differ in dependency on the batch composition. Between the batches the oxygen and carbon content can change depending on the technological procedure. The lowest density was reached in the saw teeth produced by MPIM. Therefore the content of pores was measured at the polished surface of the sample 102005-1 and the saw teeth 071106 shaped by MPIM. Besides a higher porosity the saw tooth contains also larger pores in comparison with the CIPed ceramic insert which result from a not optimal feedstock preparation or shaping technology. If we assume the highest density of batch 169a with 3.231g/cm^3 equeal 100% then the density of the saw teeth is 99.06% of it.

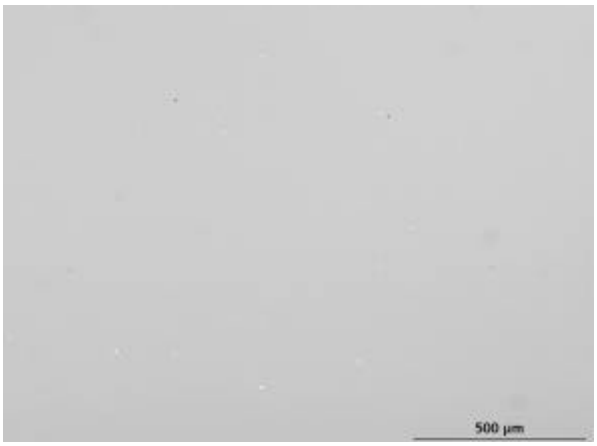


Fig.2.5-11:Polished surface of the CIPed insert 102005-1

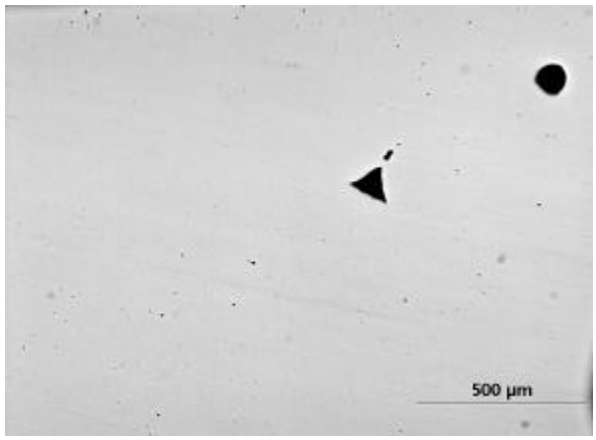


Fig. 2.5-12: Polished surface of a saw tooth 071106, shaped by MPIM

D47:" Sintered Si_3N_4 prototypes (Formatec)"

A feedstock using 500 g of SM 131(mixuture containing 50 % nano powder) was prepared for Formatec by IKTS. For testing the Si_3N_4 feedstock Formatec used both a mould to produce test bars and a mould for a small complex shaped valve (fig. 2.5-13). Injection moulding debinding and sintering was performed with good result. In the future Formatec is interested in flat Si_3N_4 parts used in production machines for the chip industry (fig. 2.5-14). Because of the big differences in wall thickness this relatively simple product becomes difficult for ceramic injection moulding technology. Using the MPIM (Medium Pressure Injection Moulding) technology and nanopowder they expected to improve the quality and reduce the flux lines over the cross section of the parts. But due to the limited amount of feedstock they could not test this big part within the project.

Fig.2.5-13: Sintered prototypes (valves) using a mixuture containing 50 % nano Si_3N_4 powder

Fig.2.5-14: Si_3N_4 parts used in production machines for the chip industry

D48:" Characterisation of prototypes on the base of nano Si_3N_4"

For woodworking cutting tools the fracture toughness could have a higher priority. On the other hand the critical chemical interaction between the glassy phase and metals as in the case of cast iron will not exist. Therefore a material with high fracture toughness and an increased amount of additives in comparison to metal cutting tools was selected for the wood cutting tools. With a mixture of 50% plasma powder and SN-E10 the fracture toughness can be enhanced in comparison to the use of pure nano powder. At the same time the ceramic material PP169 using a mixture of 50% plasma powder and SN-E10 possesses a nanostructured microstructure (fig. 2.5-15, 2.5-16). The mechanical properties of the nano

material PP169 can be seen in tab.2.5-7 in comparison to the tested standard Si_3N_4 materials and the presently used WC-Co hard metal.

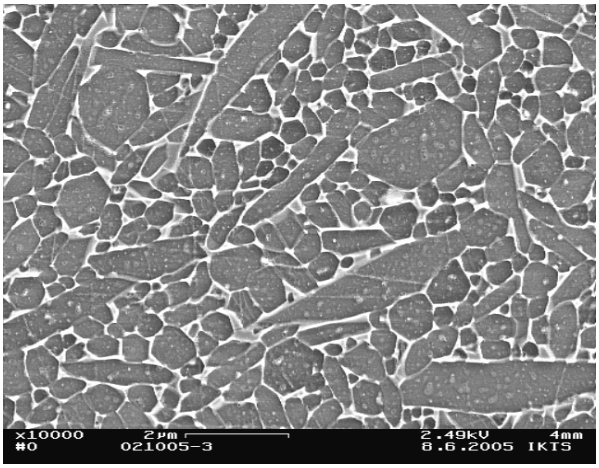


Fig.2.5-15: Microstructure of the standard Si_3N_4 material T1102

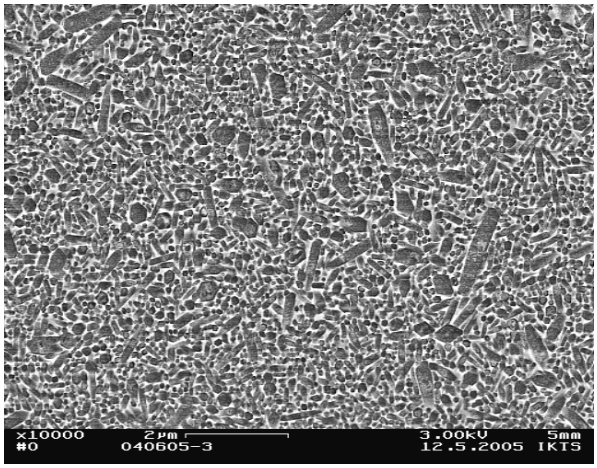


Fig.2.5-16: Microstructure of the nano Si_3N_4 material PP169

Tab. 2.5-7: Properties of the ceramics tested as cutting tools for wood working

	Content of additives, wt.%	Sintering procedure	Bending strength, MPa	Hardness, HV10	Fracture toughness, MPam $^{1/2}$ 1)
H275 (FCT)	3	hot pressing	833 ± 85	1576	4,2
H200 (FCT)	8	gas pressure	781 ± 41	1600	4,6
A118 (FCT)	30% TiN	hot pressing	884 ±22	1476	5,8
T1102 (IKTS)	4,2%	gas pressure	926 ± 89	1538	5,1
Nanoceram 2 (IKTS)	Alpha SiAlON	gas pressure	765 ±48	1739	5,4
PP169 - 50% PP	14	gas pressure	756±120	1522	4,5
WC-10.5Co 2) (Feinstkorn)	10,5		3200	1530	13,8
WC-6.0Co 2) (Feinstkorn)	6		3000	1780	10,8

1) measured from the crack length after Anstis 2) Hans Kolaska:"Pulvermetallurgie der Hartmetalle", Vorlesungsreihe, fachverband Pulvermetallurgie

The nano structured Si_3N_4 material has improved wear properties in comparison to standard Si_3N_4 materials from pure SN-E10powder. The nano materials PP169, PP170 and AY3/6 6Y8Al 1575°C could be sintered fully dense already at 1575°C and showed a lower wear rate during dry fretting in comparison to the standard materials with SN-E10 in the range of Hertzian pressure between 1000 and 1350MPa (fig. 2.5-17).

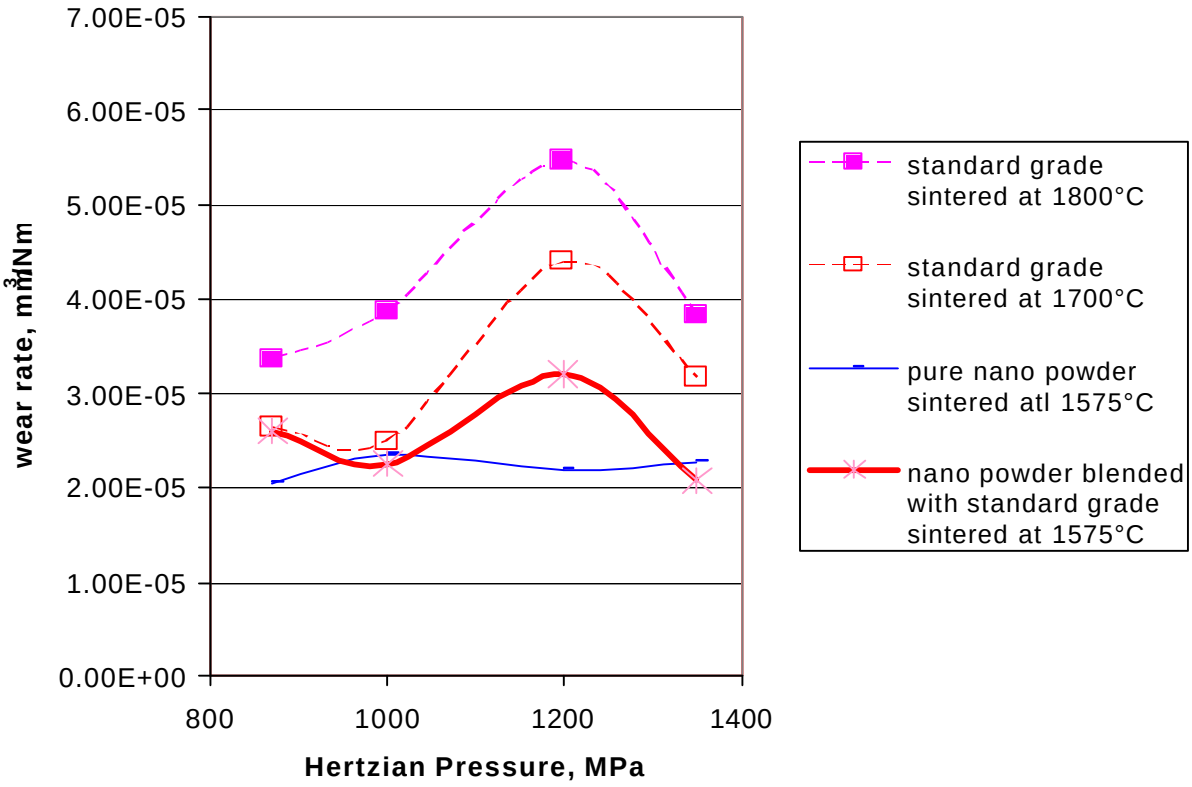


Fig.2.5-17: Wear rate in dependency on the Hertzian pressure during dry fretting at 22°C, 50% rel humidity.

D49:" Characterisation of prototypes on the base of nano ZrO_2"

With the developed feedstocks small parts with wall thickness of 0,15mm were produced via LPIM by TKC. After the optimization of the technological parameters non deformable parts could be debindered and sintered. The zirconia materials possess high bending strength. The special prototypes and the costumers in the medicine technique can not named by TKC. These special informations are confidential.

Subsequent thin walled components for applications in the medicine technique are presented in fig 2.4-22. The parts were shaped by injection moulding. They are used in the endoscopy.

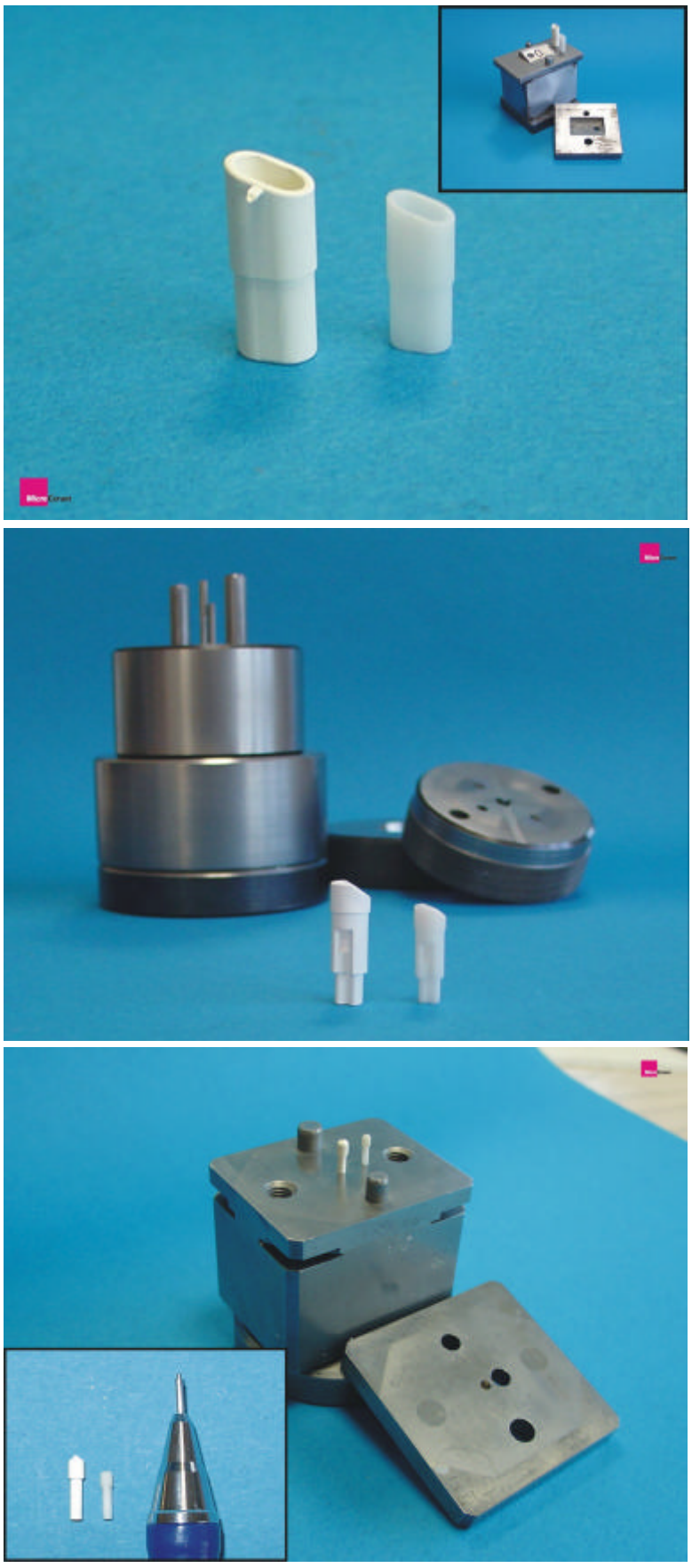


Fig. 2.4-22: Prototypes from nano zirconia for medicine technique – left part as fired, right part as sintered

M6 (22. Month): Sintered prototypes base of nano Si_3N_4 with a density >99% theoretical density; Sintered ZrO_2 prototypes with a density >99% theoretical density

The sintered prototypes from nano Si_3N_4 were described in D46. For the CIPed parts a high density and low porosity could be reached. The density of the CIPed parts was 99.5% of the highest density of the batch at least.

For the saw teeth shaped by MPIM 99% of the highest density of the batch could be reached.

In the result TKC could produce thin-walled parts (thickness <4mm) with sintering densities >99% using fine grained Tosoh zirconia via pressing and injection moulding technology which are applied in the medicine technique.

The sintered ZrO_2 prototypes using the powder TZ3Y-E were fully dense after sintering at a lower sintering temperature than materials from TZ3YS-E. Their density was <99%.

The sintered ZrO_2 prototypes using the powder TZ3Y-20A were sintered at a lower sintering temperature to get closed porosity and then HiPed to get fully dense parts (see table 2.5.3 and 2.5.4).

2.6 Prototypes / finishing – workpackage 6

Parti CIPant involved:	TKC	FCT	Formatec	Eberhard	Peitz	IKTS	RTU

Objectives

Production of prototypes from nano Si_3N_4 using different milling cutters for wood milling and prototypes from nano ZrO_2 using parts for medicine technique and surgical instruments.

Progress

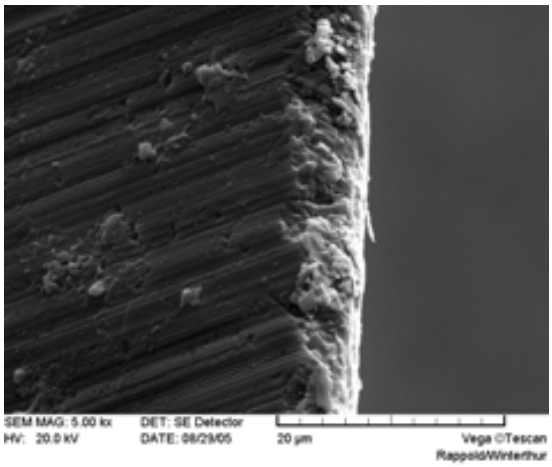
The testing in the woodworking industry took place at different customers of the partner Eberhard, Diamonde or Peitz. Different geometries of the tools from nano and standard Si_3N_4 were necessary to realise the ceramic testing in a short time during the project. Besides ceramic inserts cutter made completely from ceramic were manufactured. In addition complex shaped saw teeth were produced using MPIM technology. These teeth were clamped to the metal saw blade by Peitz using a patented assembling technology. In future applications the use of massive ceramic milling cutters can not be recommended due to the high material costs and the risk of disruption during the harsh handling of the tool in the wood working industry. We favour ceramic cutting inserts which are assembled at the metallic carrier by clamped or brazed joints. Therefore a brazing technology was developed which guarantees a strong connection between ceramic and metal. In comparison to the 12-month report the quality of the brazing joint could be essentially improved. An important precondition was that both joining steps took place in a vacuum furnace at controlled temperatures.
The finishing of the milling cutter took place by Eberhard. The machining of the cutting geometry of the brazed cutter was conducted in different steps at Walter Helipower CNC tool sharpening machine. The grinding wheels 1A1 Coolgrind D64 and 11V9 Coolgrind D25 was used. The following cutting v_c and feed rates v_f were applied for the machining of the different surfaces of the cutting edge:

Tab. 2.6-1: Griniding procedure of the metallic cutter with ceramic inserts

procedure	vc in m/s	vf in mm/min
Ship space	18	50
Cutting face front	25	80
2 times relief angle periphery	25	150
1 time relief angle periphery	25	150
2 times relief angle front	25	150
1 time relief angle front	25	200

After this machining the cutting edged from ceramic showed strong disruption (fig. 2.6-1).

Fig. 2.6-1: Cutting edge after machining with stron disruptions

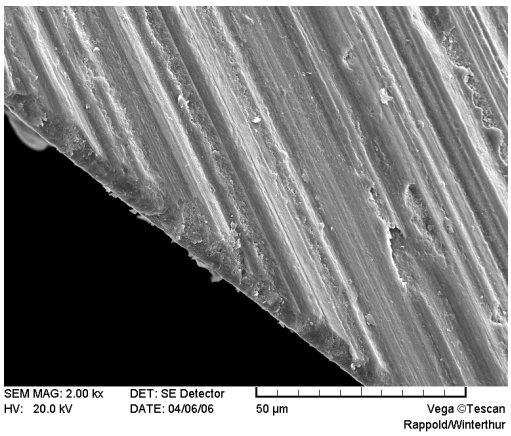


In the next test runs an improvement of the finished cutting edges could be reached by optimizing the grinding procedure. The cutters made completely from ceramic were finished after the following procedure (tab. 2.6-2) with better results than the metallic cutters with ceramic inserts (fig. 2.6-2).

Tab. 2.6-2: Griniding procedure of the cutter made completely from ceramic

procedure	grinding wheel	vc in m/s	vf in mm/min
ceramic rods - 2 times roughing	1A1 Coolgrind D64	18	60
ceramic rods - 1 times final grinding	11V9 Coolgrind D25	50	10
relief angle periphery - 1 times roughing	1A1 Coolgrind D64	50	150
relief angle periphery - 1 time final grindig	11V9 Coolgrind D25	50	10

Fig. 2.6-2: Cutting edge of a cutter made fully from ceramic after machining



Diamonde conducted also the sharpening of the milling cutter on a Walter machine "Helitronic Power Diamond". They used grinding wheels: 12V9 753 8 45 – C12 – D76, oil "Ionogrind 2 in 1" and machined with vc = 5m/s – vf =50mm/min. In comparison to diamond tools the sharpening of the ceramic tool requires only 3 hours instead of 4 hours. With the grinding process the same tolerances could be reached for ceramic and diamonde.

Deliverables / Milestones

D39:"Technology transfer to FCT"

The technology of nano silicon nitrid materials was transferred to the partner FCT. On this base nanosized materials with comparable or even better mechanical properties in comparison to materials produced by IKTS could be produced by FCT (Fig. 2.6-3). The production of nano Si_3N_4 materials has also advantages in comparison to standard Si_3N_4 materials for FCT

by the improving the mechanical properties (tab. 2.6-3), improving the homogeneity of surface colour of the sintered parts, decreasing of sintering temperature and saving of energy. FCT expected benefit of the production of nano Si_3N_4 materials for the application as cutting and milling tools (saw teeth), wear parts (bearing components, cones, nozzles and rollers).

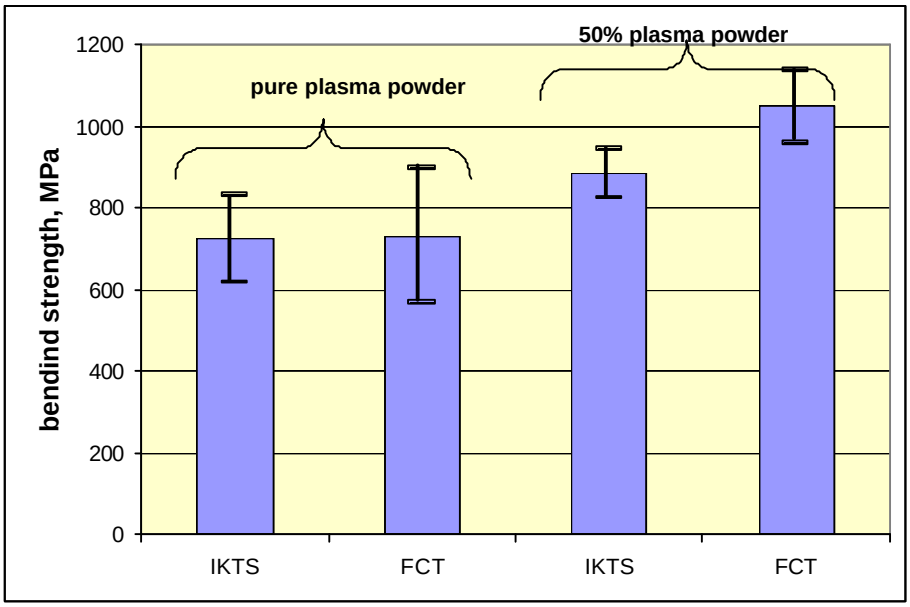


Fig. 2.6-3: Comparison of the bending strength of materials from pure plasma powder and mixtures with SN-E10 powder produced by IKTS and FCT

Table 2.6-3: Comparison of nano Si_3N_4 materials 171 (mixture of plasma powder and SN-E10), 172 (pure plasma powder) produced by FCT with standard Si_3N_4 material H0200 of FCT

	171	172	H0200
4 pt. Bending strength (MPa)	1048 +-89	732 +- 165	781 +- 41
K_{IC} (MPa $m^{1/2}$)	4.2	3.7	4.6
HV10	1558	1509	1600

D40:"Technology transfer to TKC"

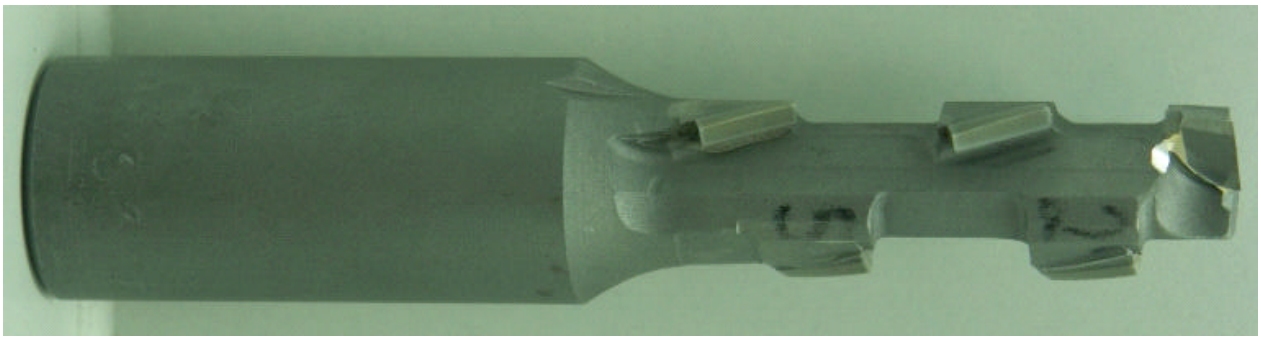
The technology transfer of the new ceramic material based on nano ZrO_2 powder of PCT to TKC makes no sense due to the quality of the grade B powder. TKC has tested spray granulate based on the grade B powder and could produce only parts with 86% density and a bimodal microstructure. The solid content of the produced feedstock for MPIM with 35vol% was not high enough for a successful processing by LPIM. But TKC could produce dense nanosized parts with thin wall thickness of 0.15mm using fine zirconia powder from Tosoh. Therefore TKC used the LPIM technology with an own binder system.

D50:" Cutting tools from nano Si_3N_4"

For testing in the wood working industry metal milling cutter with ceramic inserts (fig. 2.6-4) were produced by IKTS. The grinding of cutting edges was done by Eberhard.

Fig.2.6-4: Metal milling cutter with ceramic inserts

The following milling cutter of the geometry in figure 2.5-4 were produced:



pieces	ceramic insert	
2	standard SSN	T1102
1	SiAlON	Nanoceram2
1	SSN-TiN	A118
1	nano SSN PP169	50% SM130

In addition the following cutter (fig. 2.6-5) with bigger ceramic cutting inserts were manufactured using PP169 for testing by a selected costumer of the Eberhard Company.

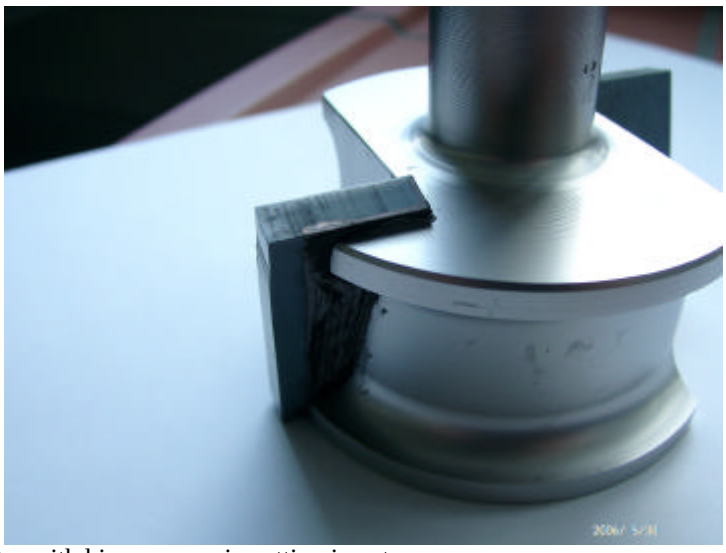


Fig.2.6-5: Milling cutter with bigger ceramic cutting inserts

Since August 2005 a series of milling cutter with ceramic inserts were produced in a furnace with controlled temperature and vacuum by IKTS. This technology allows the joining without any corrosive flux. In comparison to the results in the 12-month report the metallization took place by using a brazing foil of BrazeTec. The ceramic components, which had been metallized, were joined with the tool carrier of the metal milling cutter by using a soldering paste. Both joining steps took place in a vacuum furnace at controlled temperatures. In this process we got soldered joints without any cavities which results in strong connections between ceramic and metal (Fig.2.6-6).

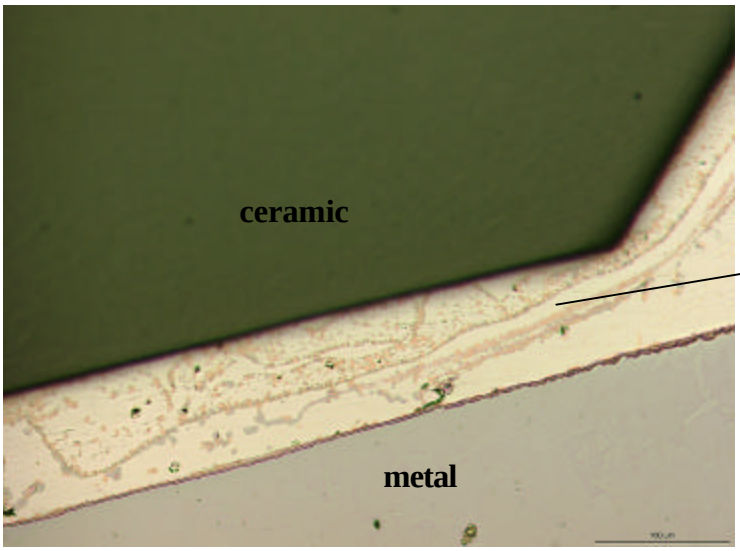


Fig.2.6-6: micrograph of a soldered joint

For special costumers 11 cutters completely made from nano or standard Si_3N_4 ceramics were produced by IKTS and finished by Eberhard (fig. 2.6-7).

pieces	ceramic component	
2	standard SSN	T1102
2	nano SSN	50% SM130
4	standard SSN	T1102
3	nano SSN	50% SM130

Fig.2.6-7: cutters completely made from nano or standard Si_3N_4 ceramics

These tools were joined with metallic shanks by shrinkage. In the joining process the metallic shank with defined dimensions was heated at 500°C and pressed on the ceramic component. The third cutting tool was saw teeth for Peitz. These teeth were produced by MPIM in the IKTS. The ceramic teeth are clamped to the metal saw blade by Peitz using a patented assembling technology.

Fig: 2.6-8: Saw teeth from nano Si_3N_4 shaped by MPIM

D51: Production of ZrO_2 prototypes"

The prototypes described in D49 were produced by injection moulding using the zirconia TZ3Y-E and TZ3YS-E for different users which produces endoscopes. The detailed information is confidential. The sinter HiP process of parts using the zirconia powder TZ3Y-20A and TZ3YS-20A is not finished. These parts will be also tested in the medicine technique.

M7 (23. Month): "Cutting tools from nano Si_3N_4 with the necessary mechanical properties and geometry; ZrO_2 prototypes with the necessary mechanical properties and geometry with the necessary mechanical properties and geometry (Determined at M4)"

As described in D50 the different cutting tools from nano Si_3N_4 were produced in the required geometries. The mechanical properties were adapted to the application in the woodworking industry.
Because a high fracture toughness is very important and a critical chemical interaction between the glassy phase and metals as in the case of cast iron will not exist we choose a material with a relative high additive content which was produced from a mixture of plasma powder with SN-E10. This material possesses a nanostructured microstructure and shows improved wear behaviour in comparison to standard Si_3N_4 ceramic. Generally the fracture toughness of ceramic is lower than those of hard metal WC-Co which are used at present as cutting tools in the wood working. But the application of high-speed- woodworking processes and the machining of chipboards and of strong melamine with hard conclusions makes also higher demands on the wear resistance of the cutting tool. The conducted tests in the woodworking industry showed that further adaptations of the cutting edge geometry are required.
As described in D49, 51 the different endoscope parts from nano zirconia were produced in the required geometries. The mechanical properties and surface quality without finishing are consistent with the requirements of the users in the medicine technique. The results show also that higher technological requirements exist using of the nanosized powders. The non optimal processing can result in defects in the nanomaterial and lower level of bending strength.

2.7 Comparison with conventional powders – workpackage 7

Parti CIPant involved	DICERAM	Formatec	FCT	IKTS	Eberhard	Peitz

Objectives

Production of cutting tools from standard Si_3N_4 and parts for medicine technique and surgical instruments from standard ZrO_2

Progress

Prototypes on the base of 5 standard Si_3N_4 materials were produced and characterized in the first project year. In addition to metallic cutters with ceramic inserts also cutters made completely from standard ceramic T1102 were produced and finished. The problems with the quality of the brazing joint between metal and ceramic could be solved. The machining and testing of cutting tools from standard materials were conducted with the same procedures as cutting tools from nano Si_3N_4 materials. The results of testing are shown in the chapter 2.8 in comparison to the nano materials.

Up to now only zirconia powder from Tosoh with surface area $7m^2/g$ are used in feedstocks for LPIM technology or as granulate for CIP technology were used by TKC. The $7m^2/g$ powder can be densified fully only at 1500°C. The level of bending strength is between 870 and 930MPa for parts produced by LPIM. In comparison the $14m^2/g$ powder can be densified already at 1450°C and delivers therefore a material with a finer microstructure and higher bending strength. While the $7m^2/g$ powders delivers after CIP and sintering materials with 702MPa the $14m^2/g$ powder delivers material with 888MPa bending strength (tab.2.7-2).

Tab. 2.6-2: sintering density and biaxial bending strength of parts shaped by LPIM and CIP using different zirconia powders from Tosoh

powder	BET surface of powder, m^2/g	Shaping method	Sintering temperature, °C	Density, g/cm^3	Biaxial bending strength, MPa
TZ-3YS-E	7	LPIM	1500	6,07	931±100
TZ-3YS	7	LPIM	1500	6,03	877±192
TZ-3YSB-E	7	CIP	1500	6,06	702
TZ-3YB	14	CIP	1450	6,02	888

Deliverables / Milestones

M8 / D15: "Manufacture of finished prototypes on the base of standard Si_3N_4"

The materials T1102 with a low content of inorganic additives and an alpha – SiAlON were produced from standard silicon nitride powders (SN-E10) by IKTS. Three standard grades at FCT were chosen additionally as prototypes. H200 is gas pressure sintered with about 8 % of inorganic additives, the two other materials (H275; A118) are uniaxially hot pressed. One of them (H275) is a silicon nitride with alumina and yttria as hot pressing additive, the other (A118) is a composite with TiN as the second phase. The finishing of the standard materials took place by Eberhard after the same grinding technology than the Si_3N_4 nano material.

M8 / D16: "Manufacture of finished prototypes on the base of standard ZrO_2"
The coarser powders TZ3YS-E, TZ3YS and TZ3YS-20A are used in the production of parts for the medicine technique at present by TKC. Prototypes exist and were used in comparison to the prototypes from nano ZrO_2.

D21:"Characterisation of prototypes on the base of standard Si_3N_4"

The standard materials differ in their properties in a wide range (tab.2.7-2). The material with the highest fracture toughness is the composite material A118 with 30wt.% TiN. The alpha SiALON possesses a very high hardness. In prinCIPle all materials are suited as cutting tools.

Table **2.7-1**: Standard Si_3N_4 materials

	Content of additives, wt.%	Sintering procedure	Bending strength, MPa	Hardness, HV10	Fracture toughness, $MPam^{1/2}$ *1)
H275 (FCT)	3	hot pressing	833±85	1576	4,2
H200 (FCT)	8	gas pressure sintering	781±41	1600	4,6
A118 (FCT)	30% TiN	hot pressing	884±22	1476	5,8
T1102 (IKTS)	4,2%	gas pressure sintering	926±89	1538	5,1
Alpha SiAlON (IKTS)		gas pressure sintering	770±45	1740	5,4

1) measured from the crack length after Anstis

2.8 Testing – workpackage

Parti CIPant involved	Diceram	FCT	Eberhard	Peitz	Diamonde	IKTS

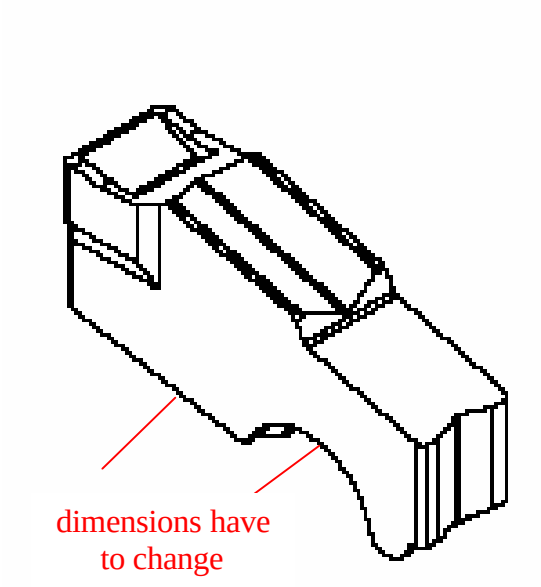
Objectives

Testing and comparison of different cutting tools from standard and nano Si_3N_4 for wood milling and parts for medicine technique and surgical instruments from standard and nano ZrO_2.

Progress

Eberhard tested the different milling cutters in milling of chipboard, MDF board and massive wood. In all cases cutting edges from ceramic showed strong flak spalling after milling. In comparison cutting edges from hard metal show only chamfering. The reason for this result could be caused in damaging the cutting edges during grinding. Therefore IKTS investigated milling cutters by FESEM. No damages at the cutting edge could be detected after grinding. Therefore the geometry of cutting edges has to adapted at the properties of the ceramic (increasing of lip angle). The use of massive ceramic milling cutters can not be recommended due to the high material costs and the risk of disruption during the harsh handling of the tool in the wood working. In future ceramic cutting inserts will be used which are assembled at the metallic carrier by clamped joints.
Diamonde had tested a milling cutter with ceramic inserts in the machining of strong melamine with hard inclusions. The ceramic inserts were assembled with the metal carrier by brazing. In the test the joint was stable. Diamonde is interested in this cheaper tool in comparison to polycrystalline diamond. The use of diamond becomes very expensive if diamond damaged at the hard inclusions of the melamine.
The saw teeth from nano Si_3N_4 shaped by MPIM were fitted in the saw blades by Peitz. A testing in the woodworking industry makes no sense due to some problems with the production tolerances. For a strong fit of the teeth in the blades two dimensions of the mould for MPIM have to change a little bit. Diamonde, Eberhard and Peitz are interested in the application of ceramic saw teeth.

Fig.2.8-1: Draw of the saw teeth with the necessary changes in dimensions



Deliverables / Milestones

D52: "Tests of the prototypes based on nano Si_3N_4"

Testing of chipboard:

The machining of chipboards was conducted over a distance of 368m using metal cutters with inserts from standard composite ceramic A118, SiAlON ceramic (Nanoceram2) and nano Si_3N_4 ceramic (fig. 2.8-1 to 2.8-5). The inserts were jointed by brazing. At the top of the cutter an insert from hart metal was attached. The brazed connection between ceramic insert and metallic shank endured the test without any problems. In the result of the test we could determine that hard metal wear more than the tested standard ceramics. But after milling test cutting edges from ceramic showed strong flak spalling at the clearance areas. Ceramic possesses lower fracture toughness in comparison to hart metal. Therefore the geometry of cutting edges would have to adapt at the properties of the ceramic by increasing of cutting angle. With this action the flak spalling can be retarded.

Fig. 2.8-1: Chipboard (3 layer x 16mm) and the used test conditions:
Router diameter Ø20mm
Spindle speed: 16.000 rpm
machine: CNC 3 spindle machine from SCM
Feed rate per teeth: 0,1875mm/U
vf.: 3m/min (very slow, because of 3 layers)
cutting distance: 368m (Diamond 5000m)

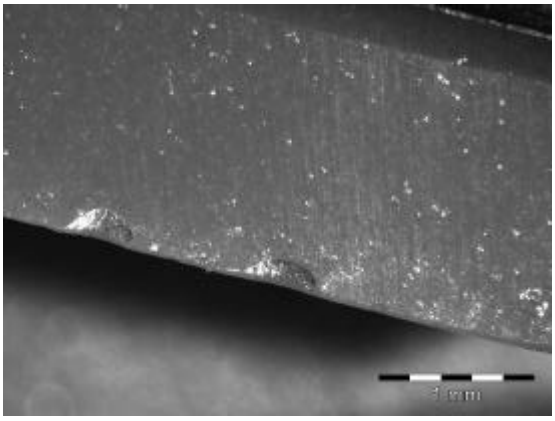


Fig. 2.8-2: Cutting egde from SiAlON – Nanoceram 2

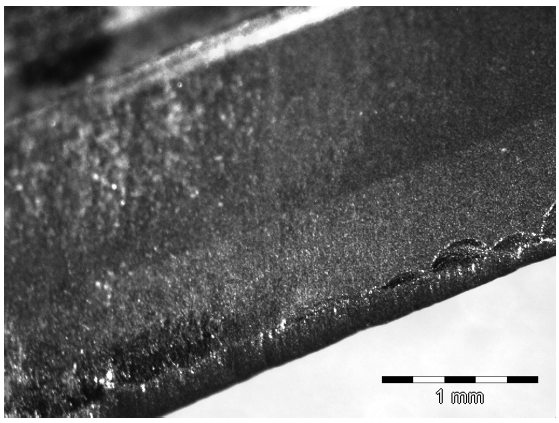


Fig. 2.8-3: Cutting egde from Si3N4 – TiN composite A118

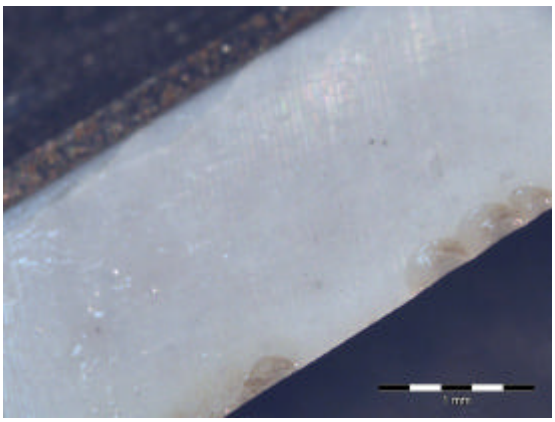


Fig. 2.8-4: Cutting egde from Nano Si_3N_4 PP169

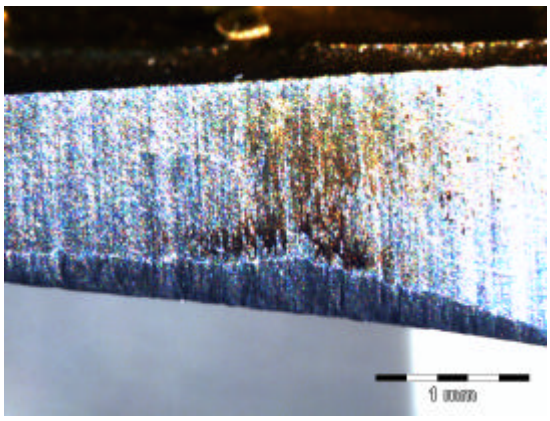


Fig.2.8-5: Cutting egde from hart metal

In addition cutters made whole from ceramic were produced by IKTS, finished by Eberhard and tested in the machining of MDF boards, which have not so big hard inclusions as chipboards. We not expected so strong stress in the cutting edges as in the machining of chipboards. In the tests (fig. 2.8-6) cutting distances of 1200m were reached. Nevertheless the cutting edges from standard and nano ceramic showed some flak spallings. In comparison the hard metal cutting edge looks better after machining. The stability of the ceramic cutting edges can be improved by changing their geometry.

Fig. 2.8-6: Diameter:16mm
Cuttingspeed: 18000 rpm
vc: 15m/s
vf: 18m/min
feedrate per teeth : 0,333mm
cutting distance : 1200m

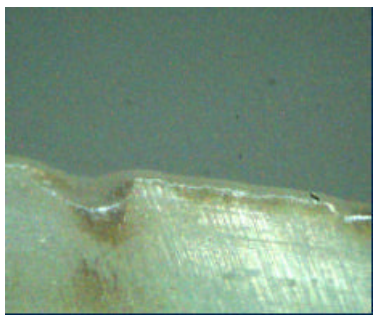


Fig. 2.8-7: Test of tool No 13 from nano ceramic 022406-2

After a crash with a piece of wood Cutting edge after grinding Cutting edge after 1200m milling



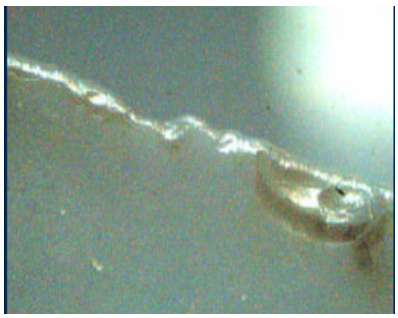


Fig. 2.8-8: Test of tool No 4 from nano ceramic 010906-1

Cutting edge after grinding | Cutting edge after 1200m milling | Cutting edge after 1200m milling

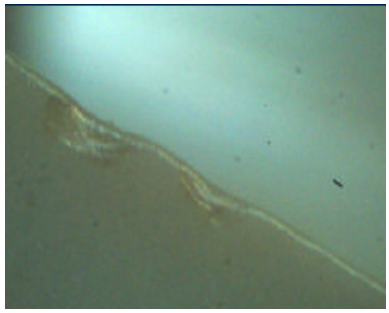




Fig. 2.8-9: Test of tool No 11 from standard ceramic 012306-8

Cutting edge after grinding | Cutting edge after 1200m milling | MDF board after machining with the tool No. 11

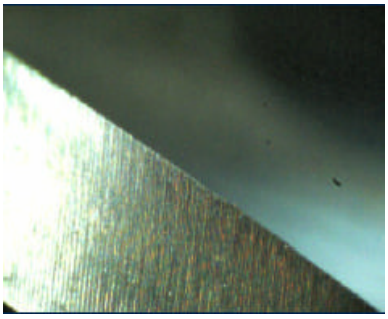


Fig. 2.8-10: Test of a tool made from hard metal HB30F

Cutting edge after grinding | Cutting edge after 1200m milling | MDF board after machining with HB30F – bad quality

For the window producer Internorm the ceramic cutter Ø14mm, length 100mm (fig. 2.8-11) was joined with a metallic shank by shrinkage. The testing was conducted in the machining of the soft massive wood of the spruce.

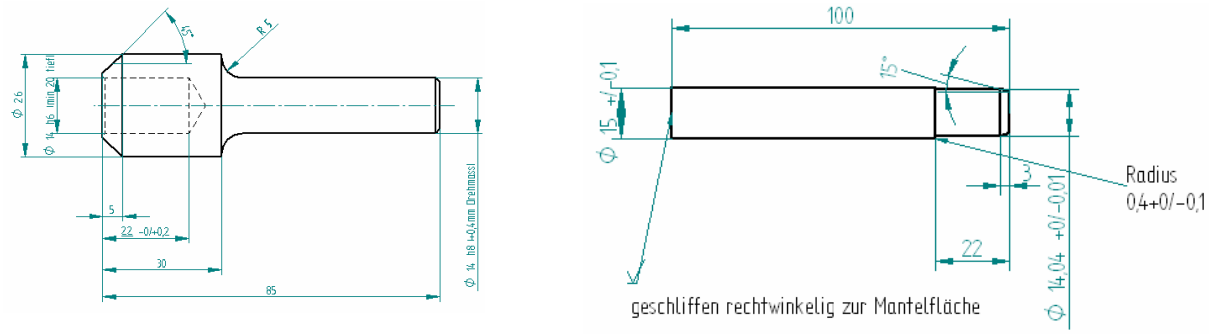
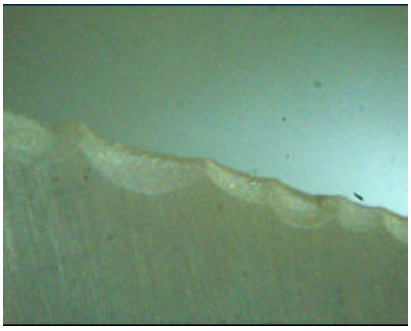


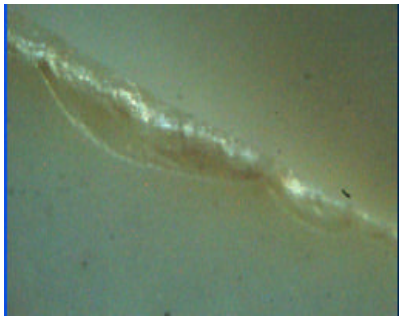
Fig. 2.8-11: Draw of the combined ceramic – metal milling cutter

There were problems in the machining of massive wood with this tool. The ceramic cutter broke after a short distance. The fitting length of the ceramic cutter was too big using the brittle ceramic. Therefore further tests were conducted with ceramic cutters which possess a shorter fitting length and under the given conditions (fig. 2.8-12). At the cutting edges of standard and nano ceramic strong chunking could be detected after 280m machining of wood.

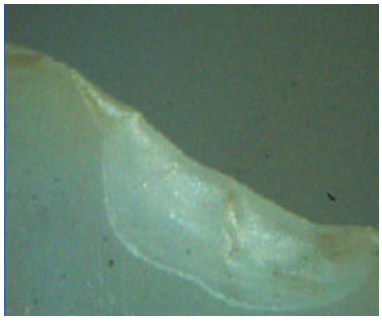
Fig. 2.8-12: Diameter:16mm
Cutting speed: 18000 rpm
vc: 15m/s
vf: 18m/min
feedrate per teeth : 0,333mm
cutting distance : 280m



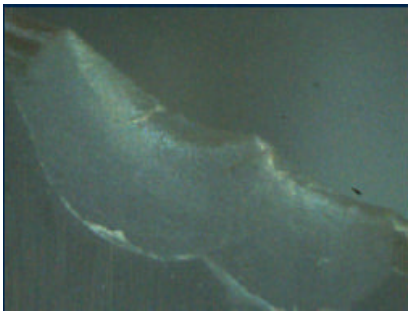
Standard Si_3N_4 T1102 - sintering 012306-7



Nano Si_3N_4 PP169a- sintering 0120605-1



Nano Si_3N_4 PP169a- sintering 022406-1



Nano Si_3N_4 PP169a- sintering 010906-1

Solid carbide in comparison

Fig.2.8-12: cutting edges after 280m machining of wood

D55: "Comparison of the tests with Si_3N_4 "

There was no difference in the results of testing between nano Si_3N_4 and standard Si_3N_4 up to now. But only short time tests with a not optimal geometry of cutting edges were done in the project. A comparison between is only possible after adapting the geometry and technology of

machining at the Si_3N_4 ceramic. In addition further investigations have to conduct after the project between IKTS, Eberhard, Petz and Diamonde.

D53: ""Tests of the prototypes based on nano ZrO_2"

Several prototypes which were manufactured using zirconia powder of Tosoh were tested with positive result in the medicine technique. These components are used in endoscopes.

D56: "Comparison of the tests with ZrO_2"

The used powder TZ3Y-E und TZ3YS-E possess crystallites of 20 and 30nm respectively. After sintering both powders deliver materials with nanosized microstructures. With the powder TZ3Y-E materials can be sintered at a lower sintering temperature. Therefore the microstructure is slightly finer. But both powders are suited for the production of thin walled parts with high surface quality after sintering. The use of the some finer powder makes higher demands in the processing.

M8: "Test results of prototypes based on nano Si_3N_4 and nano ZrO_2"

The conducted wood working test with nano Si_3N_4 are not sufficient for a transfer in the production stage. But the possibility of manufacture of nano Si_3N_4 using different shaping methods could be shown in the project.
In further tests the geometry of the cutting tools will be changed. The number of cutting edges will be increased to 4 or 5 per tool. The clearance and cutting angle will be decreased at a length of 0.4mm. The lip angle will be increased from 53° to 64° (fig. 2.8-13, 2.8-14). The clearance angle can be decreased due to the slide properties of ceramic at wood are better than of steel.
The tests with nano zirconia materials using powders of Tosoh were positive in the medicine technique. The developed materials are suited for the production of thin walled components with complex shapes and high surface quality.

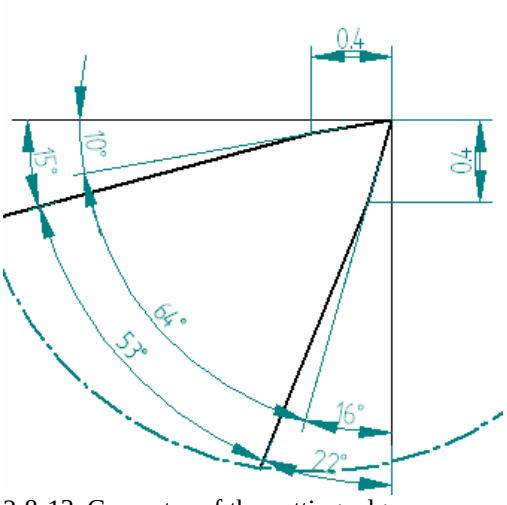


Fig.2.8-13: Geometry of the cutting edge

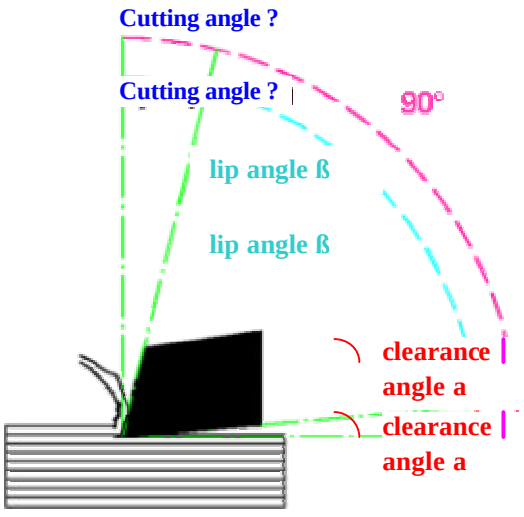


Fig. 2.8-14: Comment to the geometry of the cutting edge

Deviations / problems

The problems with the connection between Si_3N_4 ceramic inserts and metallic cutter by brazing caused a loss of time in the project. In addition the grinding of the cutters with the brazed ceramic inserts consumed a lot of time due to the machining could not take place

automatically. The tests were conducted at customers of Eberhard or Diamonde. To conduct the tests during the project Eberhard and Diamond had to adapt their test to the current production profile. Therefore special geometries of the cutters were necessary to manufacture. These consumed a lot of additional capacity and time by IKTS, Eberhard and Diamonde. These problems result in a limited testing of the prototypes. After more optimization of the cutting edge geometry and machining technology further tests at the different customers of Eberhard and Diamode are necessary. These investigations have to done in direct cooperation between IKTS, Eberhard, Peitz and Diamonde.

3 Consortium management

The communication between the partners took place by phone and e-mail between the planed meetings. In addition the coordinator organized individual meetings with Peitz, Diceram, FCT, RTU, PCT, TKC, Formatec, Diamonde, Eberhard and IVF. All partners met together at the Kick-off meeting at the Materialica 2004 in Munich, the 6-month meeting in Dresden, the 12-month meeting in Graz and the final meeting in Riga. At the meetings the partners reported their problems and results and the next tasks and steps were discussed and defined. Between the meetings two or three partners met on fairs and conferences.

Some changes in the project consortium took place. The coordinator had to organize the necessary documents for the request for amendment.

1. The Swedish Ceramic Institute SCI was incorporated into the IVF Industrial Research and Development Corporation in March 2005. The SCI will be integrated as a department within the IVF. All activities moved to IVF in Mölndal, Sweden. . IVF actively continued to refine, develop and support the Swedish Ceramic Institute's activities.

2. The French partner FORMAO was taken over by the company ALSAPLAN FURNITURES in January 2005. They carry on wood machining for furniture. But the sharpening of cutting tools, the testing of new cutting tools and research and development were transferred to the external partner DIAMONDE. This SME was able to test the new cutting tools from nanopwders for wood working and to fulfil the work of FORMAO in the project.

In the result of the amendment N°1we had got the following new partners in the project:

- Diamonde (SME) start data of partiCIPation: 10th January 2005-09-08
- IVF Industrial Research and Development Corporation (RTD performer) start data of partiCIPation: 4th March 2005

3 Diceram left the consortium due to their banc rupture. The new SME partner TKC – Technische Keramik GmbH was added to the consortium Nanoceram with the start date 1st October, 2005 to continue the tasks as producer of miniaturised parts with complex geometry and thin walls for the medicine technique. This change was attested in the amendment N°2

The project involves a large number of experts from many Organisations and SME's distributed geographically across many countries. This situation demands a strong day by day management of the coordinator and joint efforts in the consortium to solve the upcoming problems. The following problems occurred during the project and had to solve:

1 Our partner RTU took over some key functions for pre treatment of the nano Si_3N_4 - powders. A continuously working crystallisation equipment attached to the plasma reactor should deliver plasmachemical powder in suited particle size distribution and quality. Because of technical problems the assembly of the continuous crystallisation equipment has not finished yet. The partner RTU should start up this new technological equipment and evaluate the quality of the silicon nitride powder as crystallized. This modification would also affect the industrial partner PCT. PCT should proceed the crystallisation of the plasmachemical powder to produce the required amount of powder as crystallized. All these modifications were related to

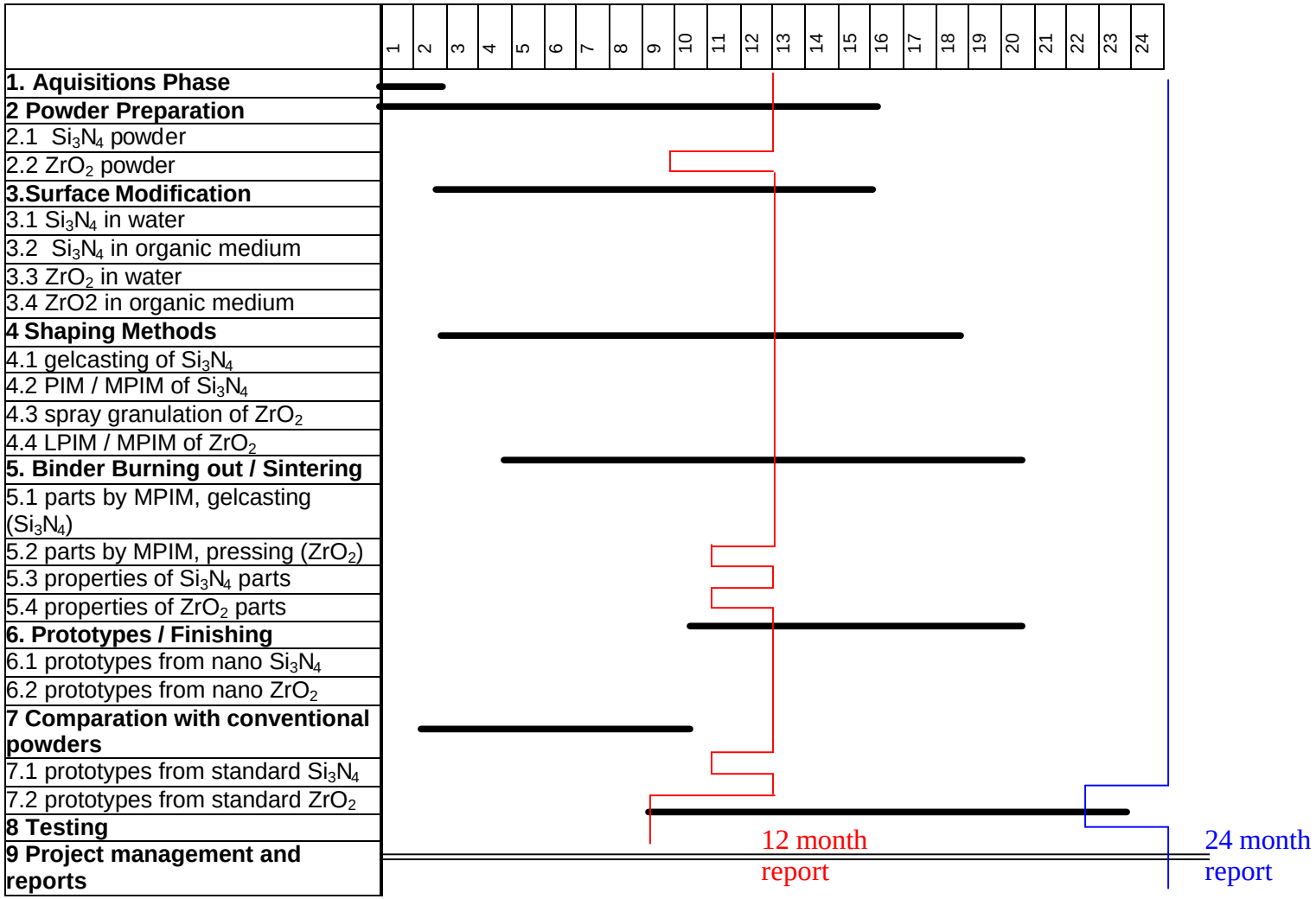
tasks in the workpackage 2. On behalf of the supply of powder for the RTD the silicon nitride powder had to be crystallised by the RTD performer IKTS. This discontinuous batch procedure is more expensive than the continuous crystallisation and additional expenses arose for IKTS. In the first year IKTS needed a capacity of 2.78 man months or 17750 EURO for the crystallization of 20kg plasmachemical powder. In the second year we had to deliver 10kg crystallized silicon nitride powder for further investigations. This means an additional expense of 1.4 man month or 8950 EURO for the crystallisation in the second year. To reduce the financial mismatch caused by these problems, we transfered a budged of 10000EURO from PCT to IKTS. To solve the problems for the second project year, the crystallisation was conducted by the TU Dresden. Therefore the volume of 10000 EURO was subcontracted from RTU to the TU Dresden. All changes had not affect the request funding by the EC. The transfer was discussed and favoured by all partner

2 The Si_3N_4 inserts for the milling cutter have to be joined with metal. The metallization could not be realized as planed by a third company due to the quality problems with the metallization of samples. Therefore IKTS had to make the metallization oneself. The ceramic components, which had been metallized, had to be brazed to the tool carrier by Eberhard. But there were some problems with strength of the joint in the first experiments. Additional investigations had to conduct to determine the cause. Therefore different joining areas between ceramic insert and tool carrier were investigated by SEM and EDX analysis by IKTS. In closed cooperation between both partners the brazing technology was optimized and the necessary milling cutters with standard ceramic inserts could be produced. These problems result in a delay. The testing of the cutting tools could not be finished. The partner Eberhard, Diamonde and Peitz expect benefit in the production of cutting tools for woodworking. Therefore the tests with ceramic cutting tools in a special geometry and type will be continued after the project. The raw parts will be manufactured by IKTS and the tests will be conducted by Eberhard, Diamonde and Peitz. All partners will pay their costs themselves.

3 In addition to some delays in the zirconia powder production by PCT caused with the providing of raw materials in the first year there were some problems with the quality of the powder grade B. The zirconia powder as delivered by PCT had besides nanosized particles a high amount of coarse particles >2µm were which form coarse grains in the sintered material. An improvement of the quality of plasma chemical produced zirconia powder could not be reached by PCT during the project. Therefore the partners IVF, Goceram and TKC have to start new investigations in the work package surface modification, shaping and sintering with two fine grained zirconia powders from Tosoh in the second year. For these work additional time was necessary which causes a delay in the transfer of the research results to the SME's Formatec and TKC. It has made no sense to transfer the results with the zirconia powder delivered by PCT to the SME's, Formatec and TKC. For this reason Formatec could not fulfill the planed tasks regarding the zirconia material in the full extent. In this connection Formatec is not able to come even close to the planed contribution of 100.000 €. The contribution of Formatec is only 44035€. This caused a reduction of EC contribution. All SME partiCIPants agreed to accept the missing costs on a pro rata basis. The SME partners guarantee the necessary transfer in order to provide the RTD performers 100% of their eligible costs incurred for research and technological development during the project. The Partner TKC conducted own investigations to the surface modification, feedstock development, shaping and sintering parallel to the

investigations of IVF. This additional activities result in the possibility to use commercially the results with the Asian zirconia powders in the production of thin walled parts with complex geometry and nanosized microstructure for the medicine technique. Nevertheless TKC has to finish the last investigations in connection with the HiPing of the parts after the project without claiming additional costs in the project.

Table 3.1: Workpackages - Plan and Status Barchart
Acronym: Nanoceram
Contract N°: COOP-CT-2004-507799



4 Other issues

There is a big interest to use results with nano silicon nitride ceramic commercially by the partners FCT, Eberhard, Diamonde, TKC and PCT. FCT will produce ceramic raw parts or finished parts from nano silicon nitride ceramic. The tests with ceramic cutting tools in a special geometry and type will be continued. If the tests show positive results Eberhard and Diamonde would produce ceramic cutting tools for their costumer in the wood working industry. At present no competition exists between the ceramic producer FCT and the tool manufacturers. The use of the results could take place in strong cooperation between the SME's (FCT production of the materials, Eberhard, Diamonde, Peitz finishing / distribution of the cutting tools).
PCT expected an increase in the production of Si_3N_4 nano powder. RTU works hardly at the starting of the crystallisation equipment to deliver the Si_3N_4 plasma powder as crystallised. This powder can be processed like conventional powder by the costumers. Then PCT has a strong lead over the other supplier of Si_3N_4 nano powder.
No commercial use is expected for materials based on plasma processed zirconia powder due the quality of this powder and the reached results during the project.
TKC will use their results with the new Asian zirconia powder and fine disperse zirconia powders from Tosoh for the production of small parts with very fine microstructures.
The feedstock and the MPIM technology using Si_3N_4 nano powder will be used by FCT, Formatec, Goceram and TKC. In the future Formatec expects benefits in the homogeneous mould filling for parts with big differences in wall thickness if they use the MPIM technology.
FCT looks for special application and products of Si_3N_4 nano powder shaped by gelcasting in cooperation with IKTS in the long run.
Goceram and Formatec are interested using the feedstock composition for zirconia powder.

Annex 1: Plan of using and dissemination of knowledge

Project NANOCERAM COOP-CT-2004-507799

Exploitable knowledge and its use

Exploitable Knowledge (description)	Exploitable product(s) or measure(s)	Sector(s) of application	Timetable for commercial use	Patents or other IPR protection	Owner & Other Partner(s) involved
New ceramic material based on nano Si_3N_4 powder for cutting tools and other wear parts	Tool for wood milling based on nano Si_3N_4 powder	Prototype Test of prototypes in defined geometry and type production	2006-07-30 is going on 2007		FCT, Eberhard, Diamonde, Formatec (IKTS)
	Tool for wood sawing based on nano Si_3N_4 powder	Prototype Test of prototypes in defined geometry and type production	2006-07-30 is going on 2007 ?		FCT, Peitz, Diamonde, Formatec (IKTS)
New ceramic material based on nano ZrO_2 powder of PCT	Parts for medicine technique based on nano ZrO_2 powder	Prototype production	2006-07-30 no commercial use		GOCERAM, TKC (RTU, IVF)
New technology gelcasting of nano Si_3N_4	Parts from nano Si_3N_4 powder produced via gelcasting	Prototype Use for acquisition and look for new markets Production	2006-07-30 2007 after 2009		FCT, Formatec In cooperation with IKTS
New technology MPIM of nano Si_3N_4	Parts from nano Si_3N_4 powder produced via MPIM	Prototype production	2006-07-30 2007		GOCERAM, FCT, Formatec, TKC (IKTS)
Feedstock of nano ZrO_2 powder for injection moulding	Parts from nano ZrO_2 powder produced via MPIM	Prototype production	2006-07-30 2007		GOCERAM, Formatec (IVF, Goceram)

The nano Si_3N_4 material using plasmachemical powder and its manufacture was patented in DE19746286 by the owner Fraunhofer Society. Base on this patent a special adaptation of the material composition was conducted by IKTS with the aim to generate special material properties for cutting tools in the woodworking. The transfer to the partner FCT shows that this nano Si_3N_4 material can be manufactured in the production scale. This result can be used by FCT to supply nano ceramic parts, which can be used as cutting tools or wear parts. FCT disposes of the needed technical equipment for a production of Si_3N_4 nano material.
The tool for wood milling based on nano Si_3N_4 powder was developed during the project. The optimising of assembling, geometry of the cutting edge and cutting parameter was started in closed cooperation between IKTS, Eberhard and Diamonde. This work will be finished after the poroject between the same partners. The saw teeth from Si_3N_4 nano material has also been optimised in cooperation between Peitz and IKTS. The partner Eberhard, Diamonde and Peitz are very interested to produce such cutting tools after the positive testing. Therefore they would use ceramic cutting inserts as sintered, which were produced by FCT. The saw teeth will be produced using injection moulding as shaping technology. Besides FCT also Formatec is interested in the production of the teeth as sintered.
If the ceramic tools can be established in woodworking industry then a market share of about 40.000 Mio € in Europe is open. At present cutting tools from ceramic were not used for woodworking. Mainly WC-Co and partially polycrystalline diamonde cutting tools are used for woodworking. Besides the technical threshold in connection with the adaptation of the cutting edge geometry and the cutting conditions to the new ceramic material also the commercial threshold exists due to the higher price of the new ceramic material in comparison to conventional hard metal. The price relation was estimated by the comparison of the prices of cutting inserts made from conventional hard metal and conventional Si_3N_4 ceramic. The cutting insert TNMA1604 produced by Ceratizit costs 7.37-8.80€ .made from WC-Co and 15.80€ made from Si_3N_4 ceramic respectively. The price for the same cutting insert made from nano Si_3N_4 would be about 20 -25€. The higher price for the cutting insert can be only compensated by higher lifetime or higher cutting speed and performance.
New ceramic material based on nano ZrO_2 powder of PCT could not developed during the project due to the quality problems of the powder. The direct commercial use of the developed freeze (investigation of IVF) and spray granulate (investigation of RTU) or feedstock (investigation of IVF and Goceram) by TKC and Goceram is not possible.
The feedstock of nano ZrO_2 powder for injection moulding which is situated for the manufacture of parts by MPIM technique including the MPIM technology was developed by IVF and Goceram and is an exploitable result. It will be used by Formatec for the production of parts which show problems in the mould filling at present. The feedstock of nano ZrO_2 will be used by Goceram to sell MPIM equipments together with the feedstock which is suited for the shaping of complex parts of nano ZrO_2 powder
The new MPIM technology of nano Si_3N_4 is also an exploitable result from the project. Besides saw teeth also other complex shaped parts can be produced from nano Si_3N_4 using the feedstock and the MPIM technology which was developed by IKTS. GOCERAM, FCT, Formatec, and TKC are interested in the use. Goceram want to supply the MPIM technique together with the feedstock for nano Si_3N_4. FCT, Formatec want to expand their product line.
The promising results with the new technology gelcasting of nano Si_3N_4 initiated Formatec and FCT to think about the introduction of this technology. They will use the results for the acquisition of new products at the market which demand the application of the relative expensive technology.

Dissemination of knowledge

Planned /actual Dates	Type	Type of audience	Countries addressed	Size of audience	responsible /involved
October 2006	Project web-site	Research, industry	All countries		IKTS, all partners
2006 / 2007	Presentation on conferences	Research, industry	Europe		IKTS, all partners
August 2006	International Wood Working Fair, Atlanta USA	industry	All countries		Eberhard
Mai 2007	Ligna Hanover	industy	All countries		IKTS, partners
March 2007	Hanover fair	industry	All countries		IKTS, all partners

In October 2006 we will finish the construction of the web site of the project Nanoceram (www.nanoceram.de). The website is used as an electronic platform for the discussion with scientists and costumers and will be updated permanently by the project coordinator.
The International Woodworking Machinery &; Furniture Supply Fair - USA® is one of the world's largest trade shows for the furniture manufacturing, architectural woodwork, custom and general woodworking industries. IWF also meets the needs of the engineered wood product, composite, wood substitute, display and store fixture, plastic fabricating, flooring, surfacing and laminating, and upholstery industries. IWF 2006 again attracted buying teams from companies of all sizes, who come from more than 79 countries to see the latest technology in machinery, supplies and services available to the marketplace. The partner Eberhard used this international fair for first discussions with potential international customers about the new cutting tools from nano ceramic. He showed first prototypes of cutters with ceramic insert which were manufactured in the project Nanoceram. The interest of the woodworking industry was high. These first contacts will be used for the selection of further customers and the conception of the next tests.
After finishing the tests we will use the Ligna in Hanover to present the new cutting tools and their benefit for wood working. At the Ligna we can meet potential costumers, which work massive wood, chipboards and other derived timber products. In addition we will use the Hanover fair 2007 to present the new technological routes for the processing of nano powders and the new nano materials. At the Hanover fair we want to target the producer of ceramic and powder metallurgical materials.

Publishable results

Publishable results were got in connection with the surface modification of different nano powders and the application of different shaping methods in the processing of nano powders. First results to the gelcasting of Si_3N_4 nanopowers were presented at the EUROMAT September 2005 with the following presentation:

> H.-J. Richter, I. Schulz, M.Herrmann; Gelcasting of Nano-sized Silicon Nitride Powder, EUROMAT 2005, Prague, 5.-8. September 2005

The following presentations were given to processing and sintering of Si_3N_4 nanopowers:

Mathias Hermann, Zhijian Shen, Ingrid Schulz; Nano Si_3N_4 materials produced by SPS and conventional hot pressing, 11th International Ceramics Congress, Acireale, Sicily, Italy, June 4-9, 2006

M. Herrmann, FhG-IKTS, Dresden; Sintern von nichtoxidischen Nanopulvern, DKG Symposium Keramik aus Nanopulvern: Verfahrenstechnik und Anwendungen, 28./29.11.2006 Erlangen

To the plasmachemical production of nano powders Mr Zalite from Plasma & Ceramic Technologies Ltd will present the following lecture:

I. Zalite; Plasmachemische Herstellung von Nanopulvern, DKG Symposium Keramik aus Nanopulvern: Verfahrenstechnik und Anwendungen, 28./29.11.2006 Erlangen

Further publications which use the knowledge will follow by the RTD partner IVF, RTU and IKTS.
Detailed information to geometry and optimal cutting conditions of the new cutting tools from ceramic will be not published. The consortium is also not ready to publicise the exact shape and the use of parts form nano ceramic which they want to produce for their costumer in every case.